MALACHITE GREEN LEUCOCYANIDE EXCITATION STUDIES WITH ULTRAVIOLET LIGHT AND HIGHLY IONIZING RADIATIONS

HENRY JOHN LOUIS RECHEN

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Excitation Studies with Ultraviolet Light
and
Highly Ionizing Radiations

ABSTRACT OF

A Thesis

Presented in Partial Fulfillment of the Requirements

for the Degree Master of Science

by

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Senior Assistant Sanitary Engineer, USPHS

The Ohio State University

1951

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Excitation Studies with Ultraviolet Light
and Highly Ionizing Radiations.

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Senior Assistant Sanitary Engineer, USPHS
B.C.E., Cornell University 1941
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A simple procedure for preparing pure malachite green leucocyanide (4,4'-tetramethyldiaminotriphenylacetonitrile) is outlined. The leucocyanide, a colorless salt insoluble in water, when dissolved in ~~ionizing~~ Polar organic solvents easily undergoes ultraviolet photolysis to form the dye typical of malachite green, with a suggested quantum yield of unity.

Typical indirect effects are observed when acetone, benzyl alcohol, acetoacetic ester, methyl alcohol, benzene or acetic acid solutions of the leucocyanide are irradiated with 200 Kev X-Rays or 4 Mev betatron gamma rays. The color produced in the irradiated solutions is determined in terms of percent transmission of light of 6400 Angstrom Units wavelength, and is compared quantitatively with standard solutions of known concentrations of malachite green oxalate in the solvents employed. Either acetic acid or dilute hydrochloric acid is added to each ~~5 cubic centimeter~~ sample or color standard to stabilize the ~~optical density~~ color of the dye formed.

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Color formation upon irradiation of the leucocyanide in dilute solution in benzyl alcohol or acetone was found to be linear with X-Ray dosage from zero to 8000 Roentgens (r), and in benzyl alcohol was found not to be critically dependent upon radiation wavelength, dose rate, wall effects or acid content during irradiation. Dye formation was found to be dependent upon the concentration of leucocyanide dissolved in benzyl alcohol. At the maximum concentration studied, 0.0525 gram moles of leucocyanide per liter of benzyl alcohol, a solution dose of 3200 r of X-Rays produced 4.20 micromoles of dye per liter, estimated to be equivalent to an ionic yield of 0.5 molecules of dye formed for each ion-pair created in the solvent by the absorbed radiation.

The leucocyanide at this concentration in benzyl alcohol, when irradiated with X-Rays or gamma rays and the amount of color formed read spectrophotometrically through a one centimeter optical path at 6400 Angstroms, possesses a radiation dose range of 100 r to 20,000 r, ± 10 percent.

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Glossary of Abbreviations

S = Solvent Mixture:

BzOH	Benzyl Alcohol.
Bz	Benzene.
AAE	Acetoacetic Ester.
Acet	Acetone.
MG-Oxalate	Malachite Green Oxalate.
MGCN	Malachite Green Leucocyanide.
MGH	Malachite Green Leucobase.
5-AcOH	5 Drops acetic acid per 5 cc.
5-HCl	5 drops 0.04 N HCl per 5 cc.
GW	Soft Glass wall containers.
SW	Silicone 'Dri-Film' coated Containers.

c = Dye concentration in micromoles per liter. (1 mole of malachite green oxalate is 2 moles of dye).

%T = Percent Transmittance at 6400 Angstroms, 1.005 cm. optical path, silica absorption cell, compared to doubly distilled water using Beckman Model B Spectrophotometer.

Adj. %T = Percent transmittance assuming %T = 100 at c = 0.00.

D = Optical Density = Log_{10} (100/Adj. %T).

K = (Sum D/sum c) from c = 0.10 to 40.0, a weighted constant from color standards according to Beer's Law.

L = (Sum net c/sum 1000rd), Specific dye yield in micromoles per liter per 1000rd, in the irradiated samples.

r/min. = Calibrated air dose of radiation in Roentgens per minute.

r = Total calibrated air dose.

d = Solvent density in grams per cubic centimeter.

rd = Adjusted air dose, r x d.

T = Temperature in degrees Centigrade.

Age = Number of hours elapsed between mixing and spectrophotometric reading of color standards or irradiated samples.

The leucocyanides, or more properly the acetonitriles, of the triphenylmethane dyes are highly photosensitive to the ultraviolet region of light energies, having an absorption coefficient greater than ten thousand at 2700 Angstrom Units in one case (H-1) when in alcoholic solution, with a claimed quantum efficiency of unity in two cases. Upon absorption of a single light quantum, the colorless leucocyanide molecule dissociates into a cyanide ion and the highly colored dye ion. It is possible to study the ultraviolet quantum yields of dilute alcoholic solutions of these substances by colorimetric comparisons with standard dye solutions*. The leucocyanide of malachite green dye is particularly amenable to study because of its considerable solubility in almost all organic solvents except petroleum ether and water, and because of the fact that upon photolysis the highly colored blue-green dye typical of malachite green is produced, a dye readily measured quantitatively in solution with a spectrophotometer at 6300-6400 Angstrom units in the region of greatest transparency of the parent leucocyanide solution.

Although sufficient quantities of malachite green leucocyanide of the desired purity could be synthesized only with the greatest difficulty, it was desired to study the effect

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Note*: Dr. J.G. Calvert, Assistant Professor of Chemistry, The Ohio State University, in conjunction with the author, expects to publish in the near future a determination of the quantum yield of malachite green leucocyanide in methanol.

of x-rays and gamma rays upon solutions containing the leucocyanide, in order to observe the degree to which a stable colored product is formed in the solutions by absorption of the highly ionizing radiations. Although it is felt that a study of the theoretical considerations involved is of greatest importance, the possibitlity that such a system might be developed to produce a reliable chemical dosimeter for highly ionizing penetrating radiations can not be ignored.

In order to accomplish the above objectives, the studies, severely limited by lack of time to pursue each serendipitous event, were confined to three major approaches:

(a) The development of a simplified and relatively rapid method of producing some grams of color-free pure malachite green leucocyanide. It required six weeks of experimentation to shorten a ten week purification procedure to two or three days per gram of pure product. The procedure is outlined in detail in Appendix A.

(b) Qualitative chemical tests of the nature of malachite green dye, its leucobase, carbinol, and the leucocyanide in various degrees of purity and in whatever solvents it was anticipated such knowledge might be useful. Appendix B tabulates the chemical structures referred to by common names in the text, and briefly lists their technical names and pertinent properties. Additional information is also included concerning the solvents investigated. This section of the study included qualitative ultraviolet investigations, a close survey of all pertinent literature of the previous

half-century, and a determination of spectrophotometric methods to be employed for color measurements.

(c) When sufficient leucocyanide was prepared, the x-ray and gamma ray investigations were commenced. It quickly became apparent that these tests would consume the entire output of the purification procedure, and it was necessary to use compound not fully freed of undesirable impurities. It must be realized that until the second series of x-ray tests was prepared, only two hundred milligrams of the leucocyanide had been purified and identified.

It is most desirable that malachite green leucocyanide be studied, since it is quite stable in the presence of the acids required to stabilize the color of the dye produced from it photochemically or radiochemically. It is not readily oxidized or reduced, even at high temperatures in most solvents. The photochemical effect (a direct absorption process) appears to be quite independent of solvent pH, especially if the solvent is rather acid. Finally, the compound in solution is entirely colorless in visible light. The reader will quickly find that few other known dye-producing chemicals can boast such an array of stable chemical properties.

Historical Background

Malachite Green Leucocyanide (4,4'-tetramethyldiamino triphenylacetonitrile) was first reported in 1900 by Hantzsch and Osswald (H-2) as one of a series of leucocyanides of the triphenylmethane dye family. The photochemical properties were originally studied by Lifschitz and Joffe about 1920 (L-1)(L-2)(J-1). The crude leucocyanide is easy to prepare. However, in order to study its photolysis and phototropy, it is necessary to prepare the compound almost absolutely free of excess cyanide and traces of the original dye. Varying degrees of success may be found in the literature, but little research was done with this compound due to the tedious and expensive (as regards final yield) methods employed for purification. Fortunately, dilutions on the order of one hundred micromoles per liter are quite sufficient for photochemical studies, and thus one need only prepare one-tenth of a gram or so, enough for analysis and study. In 1936, after a ten-week purification showing extreme persistence, Harris, Kaminsky and Simard (H-1) were able to carry out a complete quantum yield study of both crystal violet and malachite green leucocyanide, and proposed malachite green leucocyanide as a precision actinometer (H-3). Their determinations showed a quantum yield in dilute alcoholic solution of unity from 2537 Angstroms to 3130 Angstroms, with a temperature coefficient of unity from -78°C to 30°C. Unfortunately, they employed malachite green leucocyanide as an actinometer to measure the quantum

yield of monochloroacetic acid photolysis at 26°C to 29°C, and found it to be 1.07 ± 5.5% for the 1N acid, in agreement with Rudberg (R-2). Later work has demonstrated that chlorine-acetic acid production by photolysis of monochloroacetic acid is variable, and a more correct figure is probably a quantum yield between 0.3 and 0.6 (L-3). Thus considerable doubt reflects upon the entire determination as carried out by Harris, Kaminsky and Simard. Their cross-determination with crystal violet leucocyanide was in agreement with the earlier work of Weyde and Frankenburger (W-1).

In 1939, an extension of the investigations was made by De Gaouck and Le Fevre (D-1) in which they observed the familiar dark reaction (phototropic color-fading after photolytic color formation), measured the conductivity changes in the process, and made a determination of the dipole moment of the dye. The dark reaction was also observed by Germann & Gibson (G-2) with a product purified for five weeks. In 1941 Lyman Chalkey (C-1) employed malachite green leucocyanide as a basic material for a photochemical process of high yield in preparing organic mercury derivatives of basic triphenylmethane dyes.

Malachite green dye has been studied more carefully because of its commercial implications. Its stability is derived from its resonant ionic structure when in solution (C-2). Thus, although the dye structure has a greater

absorption coefficient throughout the ultraviolet wavelengths of 2250 to 6500 Angstroms than has the leucocyanide, the photolysis of the dye caused by absorption of these quanta appears to be miniscule in degree by comparison. Evidently the absorbed energy is quenched in the dye molecule by nonphotolytic conversion to heat energy or by fluorescent emission. When exposed for two months aerobically to sunlight, a solution of malachite green oxalate was oxidized 25% to Michler's Ketone; anaerobically, the dye was reduced to its leucobase (I-1). The stability of the dye structure should give it the ability to protect systems in which it is dissolved. As an example, both the dye and its leucobase are good negative catalysts for the autooxidation of acrolein, styrolene, and other easily oxidized systems.

The reaction of malachite green with hydroxide forms its colorless carbinol (color base), which is photosensitive in the ultraviolet region to form the dye ion (A-1), which then fades to the carbinol by a dark reaction. The absorption spectrum in the ultraviolet of the dye carbinol is essentially identical with that of the leucocyanide (N-1).

The dye leucobase is the reduction product of the dye or the carbinol. In acid solution it is readily oxidized to the dye. The leucobase is not photosensitive.

A search of the literature revealed no parallel type of research in which a quantitative yield of color was to

be produced by an indirect radiochemical effect in a single phase photosensitive non-aqueous system. In fact, it was difficult to find many irradiation studies of non-aqueous systems. Many systems are offered in which the dye is employed as an indicator of the quantity of chemical change produced, but in none is the dye used as the indicator of its own chemical alteration. This is due to the fact that dye structures are inherently quite stable; a tremendous dose of radiation is required appreciably to alter the color of the dye. In addition, the very conditions that make the dye color stable for measurement are those that prevent the tremendous changes necessary for interpretation. Any good textbook on x-ray applications usually describes the chemical effects of radiations, (G-1,p.1345)(G-3,p.215) and in the lists of such changes one will find many in which a dye could be employed as an indicator of the change produced. Typical are the following:

(a) Folin's reagent is employed by Day & Stein (D-2) colorimetrically to estimate the production of phenols by x-rays from benzene plus sodiumbenzoate in aqueous solution.

(b) The deoxygenation of aqueous gels and liquids by the action of x-rays can be demonstrated by the fading of methylene blue dye (D-3).

(c) Brom cresol purple color changes were employed

to indicate the chain reactive release of acids from an aqueous 2-phase chloroform system subjected to x- and gamma rays (T-1).

In the above three examples, the dye need not have been employed. Its use was dictated by the extreme sensitivity of the colorimetric method of measurement. Thus it can be seen that the triphenylmethane dye leucocyanides provide a uniquely stable dye precursor which is highly unstable when subjected to the proper excitative phenomena; the formation of the dye is a quantitative measure of a specific alteration in the leucocyanide structure, and if a high yield of measurable color can be produced radiochemically, a new type of chemical system is available for the study of the nature of radiation-caused chemical reactions.

The usual method of reporting a chemical effect produced by ultraviolet light is by means of the quantum yield, that is, the ratio of the number of molecules altered to the number of ultraviolet quanta absorbed in the system. If a material in solution is being studied, a solvent is chosen which absorbs the light to a very small degree, so that it can be assumed that all quanta absorbed were absorbed in the solute molecules. A quantum yield of unity would indicate that a specific energy state in a molecule is absorbing the ultraviolet quantum and is always altered in a specific manner. If the quantum yield exceeds unity, a chain reaction is indicated; if less than unity, competitive processes are interfering (B-1,p.34)(G-1,p.1145). Similarly, the usual practice in reporting radiochemical alterations has been to estimate the ionic yield, the ratio of specific altered molecules produced to the number of ion-pairs assumed to be created in the system by the absorbed radiation. Lea (L-4) discusses this computation at some length. Contrary to what obtains for the quantum yield, an ionic yield in excess of unity does not essentially indicate a chain reaction, but may suggest that some of the absorbed energy assumed wasted in ion-pair production may actually appear in excited states of the original molecules or their ionized products, and thus enter into specific reactions. Although it appears that in aqueous solutions this possibility is minimized, (O-1,p.633)(L-4), in some systems there appear to be indications of such a

mechanism, such as that discussed by Dale & Davies recently (D-4). Many organic solvents, especially the cyclic conjugated systems, possess a large number of semi-stable excited energy states, and one can not assume that radiation effects in these solvents will be directly analogous to those in aqueous media, especially since these cyclic compounds act as energy quenching protective systems in aqueous media and in non-aqueous media, even protecting identical neighboring molecules by a quenching process ([illegible]-1).

In ultraviolet fluorescence studies of dilute organic solutions, it was long recognised that an energy transference process occurred over a chain of solvent molecules to a solute molecule. The possibility of producing a similar effect by means of gamma ray excitation of the solvent was first tested exhaustively by Kallmann (K-1)(K-2), who also discusses the possible mathematics of the process. Unfortunately the author does not discuss the possibility that the effects observed were primarily due to the chemical or excitative effects of free radicals and ions possessing a relatively large amount of kinetic energy, released in the solution by absorbed radiation and its secondary effects, rather than due to the non-chemically reactive energy transference process.

Almost all organic liquids are fluorescent to some degree when excited by the proper wavelength of ultraviolet

light. It has also been observed that the same organic solvents, when very pure, fluoresce only slightly when excited by more energetic radiation (x-rays, gamma rays, beta or alpha particles). However, when a small amount of fluorescent impurity is introduced in solution at a concentration of 0.01 to 0.0001 gram moles per liter of solvent, fluorescence of the solution is enormously increased, the effect being apparently identical to that observed for similar solutions when excited by ultraviolet light (N-2, and references cited in this article). The fluorescence, which is typical of the solute, not the solvent molecule, is observed to be a maximum at a critical concentration. At lesser concentrations a decrease is noted, explained by a decrease in probability of transmission of excitation energy from solvent to solute molecules. At greater concentrations the decreased fluorescence is explained as an increased probability that two solute molecules will mutually quench the excitation energy without fluorescence.

It is obvious that a specific amount of energy cannot be transferred from an excited solvent molecule to a ground state solvent or solute molecule unless the molecule to which the energy is being transferred is capable of absorbing that amount of energy. In addition, the molecule transferring the excitation energy must be capable of holding the energetic state for a finite length of time without quenching

it by an internal degradation process into heat or by chemical decomposition. By a knowledge of the ultraviolet absorption, photolytic and fluorescence data of the specific solvent molecules and solute molecules studied, one should be able to predict the probability of occurrence of such an energy transference process. In Doctor Kallmann's studies, those solvents which did not possess absorption (excitation) bands in the near ultraviolet region did not appear to transfer an appreciable amount of energy to solute molecules capable of fluorescence when excited by those amounts of energy. If the solute fluorescence actually was being excited chemically, that is by free radical and ion fragments diffusing from the paths of absorbed ionizing radiation, one would expect the solute fluorescence to be relatively indifferent to the chemical structure of the solvent molecules, as long as those molecules consisted of somewhat the same proportions of carbon, hydrogen, and oxygen, and thus fluorescence should occur even in solvents not having the proper excitation bands for energy transference.

An excellent discussion of the indirect chemical effects of absorbed radiation in aqueous solutions is given by Lea (1-4). It would seem that if the effects observed are *not* due to the ionizing power of the radiation absorbed in the solvent but are due rather to its excitative effects on the solvent, it would be quite difficult to observe which process predominates, unless one knew which process most

probably affects the specific solute studied.

If the energy transference process predominates, for any one solvent the least concentration at which a maximum effect on solute molecules is observed should be generally indifferent to the exact solute molecule, provided each type of solute molecule responds to the same excitative mechanism. In other words, for any one solvent, the least gram moles per liter of solute at which the maximum effect is observed should be independent of the solute itself. Observe that if the effect is predominantly due to ion-pairs created in that solvent by the absorbed radiation, the exact same rule should apply. There is another criterion which might be employed to separate the one effect from the other - for a given solute, if the change observed is due only to ion-pair chemistry, the effect should depend more on the concentration of the solute molecules in the container rather than upon the molar concentrations in the various solvents. It can be seen that the reverse would be true if the effect observed is critically dependent upon the *number* of solvent molecules through which an excitative event is required to transfer itself.

In Kallmann's work, the least concentration in gram moles per liter at which anthracene gave maximum fluorescence appeared to be generally independent of the solvent employed, indicating that excitation of the anthracene

molecules was more probably due to chemical excitation rather than to an excitative transference process between solvent and solute molecules. However, his results are not numerous enough to permit definitive interpretation, and undoubtedly contain systems involving one or the other or a mixture of both mechanisms. Due to the side effects tending to conceal clear cut indications, it is doubtful if a full interpretation can be made from the present supply of limited experimental data.

While Kallmann employed fluorescent solute molecules for his studies, it was evident that malachite green leucocyanide provided an equally excellent energy trap for a range of ultraviolet excitation energies. The absorption of a specific excitation event is recorded by the coloration of the dye molecule, and can thus be measured colorimetrically. Provided the degree to which the released cyanide ions recombine with the dye ions to reform the colorless leucocyanide is small, and provided other decoloration mechanisms are low, percentagewise, a definite colorimetric effect proportional to the amount of absorbed radiation should be produced. If the mechanism producing the coloration is the energy transfer process, it could produce an ionic yield in excess of unity in an ideal solvent, even without a chain reaction occurring. Similarly, a chemical ion-pair type of excitation should produce at best an ionic yield of unity, probably much less. It was realized that due to the complexity of the problem,

since it was apioneer research, it was quite probable that time might not permit sufficient research to provide interpretable results.

Ultraviolet Light Experimentation

A search of the pertinent literature and a series of qualitative ultraviolet irradiation tests were employed to indicate the nature of the various solvents and malachite green derivatives that were used in the x-ray and gamma ray irradiation experiments.

Hantzsch & Osswald, Lifschitz & Joffe and the other authors all demonstrated the fact that ultraviolet photolysis of malachite green leucocyanide requires solution in an ionizing solvent (C-1)(D-1)(G-2)(H-1,2,3)(J-1)(L-1,2)(M-1). Photolysis to the typical blue color occurs in absolute methanol or ethanol, glacial acetic acid, acetone, benzyl-alcohol, and acetoacetic ester. It will not occur in dilute or concentrated mineral acids, benzene, ethyl acetate, carbon tetrachloride, chloroform, ether, etc. After photolysis, a fading "dark" reaction was found to occur to varying degrees, accelerated by water, hydroxide or cyanide. Several explanations were given for this mechanism by the above cited authors, some claiming recombination to form the original leucocyanide, hydrolysis to form the acidolytic carbinol, also light sensitive, or the formation of a third colorless light sensitive substance.

It was noted by the author that in the non-ionizing or weakly ionizing pure solvents, the dye malachite green oxalate also faded. This is satisfactorily explained by assuming the dye is more soluble in these solvents as a colorless

non-ionic salt rather than as the colored ionic salt, and the shift is predominantly toward the colorless compound. This system in benzyl alcohol showed no light sensitivity at 2537 Angstroms, except perhaps an increased degree of fading, which could be due to a photolysis of the solvent, not the dye.

The most noted feature was that the dissolved dye completely faded in those organic solvents in which photolysis did not occur. In solvents such as benzyl alcohol, where leucocyanide photolysis and phototropy both occur, the dye also showed a great tendency to fade. In the highly ionizing solvents, little or no dye fading occurred except after a relatively long time. One can relate photolysis and dark reaction to the ability of the solvent to preserve the dissociation of the colored dye molecule. This type of phototropy can always be partially reversed by the addition of a trace of acid, and is completely reversed by addition of sufficient acetic (dry) acid or dilute HCl.

If the leucocyanide contains a free cyanide impurity, a phototropy occurs after photolysis that proceeds in the presence of acid. This must be the reformation of the original acid-stable leucocyanide, since the phototropic product is light sensitive.

If the phototropy is caused by excess hydroxide, the colorless carbinol is formed, which can be completely reconverted to the colored dye by the addition of acid, and

which is also highly light sensitive.

Germann and Gibson (9-9) noted that when stored in 80% aqueous ethanol, the leucocyanide hydrolysed completely to the dye in the dark. This thermal reaction is found to be even more marked in acetone. Water and possibly a trace of acid appear to be necessary for catalysis of this reaction.

From the preceding, one may state that the ultraviolet photolysis of the leucocyanide appears to be a single quantum dissociative process; the color formed is dependent upon the ionizing power of the solvent. If the solvent (i.e., benzene) shows no association with the freed cyanide ion, recombination to the original leucocyanide will immediately occur and no photolysis will appear to have occurred. After photolysis, a dark reaction will proceed to some extent if the solvent possesses a low order ionizing power. Impurities such as hydroxide and cyanide will cause dark reactions to the unstable light-sensitive carbinol and the acid-stable light sensitive leucocyanide respectively, the later reaction going even in the presence of acid. If the solvent is capable of reacting with HCN under the given conditions (acetone forms the acetone cyanohydrin readily), a thermal decomposition of the leucocyanide may take place. In addition (I-1) a slow ultraviolet sensitized decomposition of the dye is possible, aerobically to lose a phenyl group to form Michler's Ketone (para-dimethylaminobenzophenone), anaerobically to reduce to the leucobase. The dye itself

(C-2) is manufactured by the acid-catalyzed oxidation of the lanosones. For the structures and characteristics of the various compounds referred to in the text, please refer to Appendix B.

X-ray and Gamma Ray Experimentation

(1) Sample containers:

All of the liquid samples irradiated were aerobic, 5 cc. portions in soft glass, glass stoppered, cylindrical shell vials (used because of ready availability), of the following dimensions:

Outer diameter	10.3 millimeters
Inner diameter	7.1 millimeters
Internal, bottom to stopper	50 millimeters
Average liquid depth	28 millimeters.

Each sample vial was individually wrapped in a single layer of thin opaque red paper, in order to prevent accidental absorption of stray light. Spectrophotometric examination showed that the red coloring matter, if accidentally absorbed by the solvents employed, could not interfere with measurement of the typical color of the leucocyanide photoproduct. All vials were washed in slightly acid acetone-methyl alcohol before use, and air dried.

(2) Radiation sources:

X-rays were obtained from the 250 kilovolt General Electric Tungsten Filament x-ray machine belonging to the Department of Veterinary Medicine, Ohio State University. For all runs the machine was operated with the beam horizontal, at 200 kv., 10 ma., with no external filter. Dose rate was altered according to the inverse square law. Four test vials were irradiated simultaneously side by side, occupying about two-thirds of the beam's effective width. The vials were placed vertically on the edge of a wooden

table, in such a way as to minimize scatter, in a reproducible geometry, the axis of the cylindrical vials being perpendicular to the axis of the x-ray beam.

The air dosage in Roentgens (r) was computed from data provided by a private communication from Major Norair M. Lulejian, USAF, who carefully calibrated the machine employing a Model 70 Victoreen Air-wall r-meter, condenser type, which in turn is calibrated at six month intervals by the U.S. Bureau of Standards. In a two-minute exposure, results were reproducible within ± 2%. The x-ray beam was homogenous within ± 2% over its effective width.

Air dose rates, in r per minute were computed according to the following formula:

$$\text{Air dose, r/min.} = 84 \times (50/D)^2$$

where D = distance in centimeters from focal point to axis of test vial.

All x-ray tests were carried out at room temperature, 22-25°C.

The gamma ray source was the 4 Mev Betatron belonging to the Ohio State University. The primary beam is essentially monochromatic, but at the point close to the doughnut where the test vials were irradiated, a large portion of the radiation consists of beta particles and brehmstrahlung of very inhomogeneous character.

All samples were irradiated at approximately identical

geometry, the location being 9 cm. from the doughnut to the axis of the sample vial, in the median plane of the emergent beam. Due to the vibration of the magnet, it was necessary to insert the sample taped to a brass probe, mounted from the floor. In addition, it was necessary to operate a blower to keep the sample temperature below 30°C during irradiation. Due to these factors, geometry could only be considered reproducible within ± 10% air dosage.

Calibration was done with the Victoreen r-meter, and the following data recorded:

Location	Air Dose	Remarks
(a) 9cm. from doughnut (center of test sample)	53 r/min.	No shield
(b) 9cm. from doughnut (center of test sample)	40 r/min.	r-meter shielded with glass vial, similar to test vials.
(c) 7½cm. from doughnut	43 r/min.	No shield
(d) 9½cm. from doughnut	33 r/min.	No shield

It was therefore assumed that the average air dose at the sample volume could be taken as 45 r/min., with a probable accuracy of ± 10% reproducibility.

(3) Sample preparation:

For any one set of x-ray runs, a single batch of chemical and a single mixture of solvent was employed. It was assumed that the reagents were 100% C.P. reagent in all experiments unless specifically otherwise stated.

All leucocyanide dilutions were handled under reduced illumination, stored in brown glass bottles in a light proof locker. No acid was added to the samples until shortly before irradiation. If a series of dilutions was to be irradiated, all were mixed from a single stock solution. Acid was added to the stock solutions before apportionment to the individual test vials. The acids employed were either C.P. Glacial Acetic Acid or 0.04N aqueous Hydrochloric Acid. Stock solution dilutions were made volumetrically with an accuracy of ± 2%. For reproducibility from batch to batch of chemical and solvent, it was assumed that the degree of error was ± 5%. All chemicals were weighed to within the nearest 0.0001 gram, ± 0.0002 gram. Appendix C is a list of the reagents employed for these experiments. All color standards and test samples were stored and transported under identical conditions, between 20 - 25°C.

(4) Colorimetric readings in terms of percent transmissivity (T%), were made in a matched pair of quartz Beckman 1 centimeter square cells in a Model B Spectrophotometer (National Technical Laboratories, South Pasadena, California) belonging to the Department of Bacteriology, The Ohio State University. The comparison blank was doubly distilled water, and each sample was measured twice before recording. The quartz cell had an internal path length of 1.005 cm. It was found that in reading percent

transmissivity, the reading of any one sample was exactly reproducible, but in order to allow for small variations in adjusting the scale to zero, a reading accuracy of ± 0.1% transmissivity was assumed, where % transmissivity = 100 x I/I_0. It can be seen that this introduces only a very small error in the result.

Experimental measurements demonstrated that

(a) For the solvents employed (Methanol, Acetic Acid, Benzene, Benzyl Alcohol, Acetone and Acetoacetic ester) the wavelength at which color was most intense due to the malachite green oxalate dye, the leucocyanide's photoproduct, and the colored radiochemical decomposition product of both the leucocyanide and the leucobase of the dye was 6300 - 6400 Angstroms. 6400 Angstroms was chosen as the wavelength for all readings, using a sensitive bandwidth of 50 - 75 Angstroms. Through the visible spectrum all of the above colored products were indistinguishable spectrophotometrically.

(b) The pure solvents, with or without acid addition, aged over a period of days after being opened, appreciably decreasing the percent transmissivity (% T) at 6400 Angstroms. Therefore a solvent blank was made for each test run, and it was assumed that the pure solvent aged to the same extent in all test samples and color standards as in this blank which was prepared at the same time as the others were mixed. It was necessary to make this assumption arbitrarily. Actual x-ray tests demonstrated

that the aging of the solvent did not appear to be altered in % T at 6400 angstroms during the time of irradiation, as compared with a similarly treated non-irradiated solvent blank.

For the purpose of interpreting the results as read in terms of % T, the original % T was converted to an adjusted % T based on the solvent blank having a % T of 100.0%.

Adjusted % T =(100.0/Solvent Blank % T) x measured % T.

Then, assuming Beer's law to hold, the color reading was computed in terms of D, where D = optical density:

adj. % T = $100 \times I/I_o$

Antilog D = I_o/I = 100/adj. % T

Beer's Law $I = I_o\ 10^{-ecd}$

$D = e\ c\ d = 2 - \log_{10}$(adj. % T)

where e = a constant, the absorption coefficient.

c = solute concentration in gram moles/liter.

d = light path length in centimeters.

I_o = light intensity transmitted by solvent blank.

I = light intensity transmitted by sample.

Using a circular slide rule, the adjusted % T and D could be found in a single operation, setting up original % T measured.

(5) Color standards:

(Refer to Figure 1, Color Standard Curves).

In each solvent, color standards were prepared by serial volumetric dilutions from aged (7 or more days old) stock solutions of malachite green oxalate. The stock solutions contained 50 micromoles per liter of malachite green oxalate (0.0463 grams per liter), it being assumed that these stock solutions contained 100 micromoles per liter of dye when in complete solution. The dye was weighed ± 0.0002 gm, and 1 liter of each stock solution was prepared.

It was found that the optical density of the dye at 6400 Angstroms depended on the age of the solution, and the ionizing power of the solvent. In pure benzyl alcohol, the dye faded almost completely; while in acetone very little fading was noted. Therefore, when the irradiated leucocyanide sample optical densities were determined, acid varying from 1 drop glacial acetic acid to 5 drops 0.04 N HCl per 5 cc. sample was added before reading, before or after irradiation. Similarly, color standards were mixed at the same time, and acidified in an identical manner in an attempt to give comparable color yield determinations. It was realized that probably the largest error in computing color yields was in matching the optical density, D, to the proper color standard curve.

Fortunately, in the range of dye concentrations

employed, Beer's law was obeyed, a log-log plot of each series of dilutions being a straight line from less than 0.10 micromole per liter of dye to beyond 40 micromoles per liter, having a slope obeying the law:

$$D = K\ c$$

where c = dye concentration in micromoles/liter.
D = Optical Density
K = A constant.

The effect of varying acid addition from one drop of glacial acetic acid to 5 drops 0.04N-HCl per 5cc. of sample was to increase the value of K by approximately one-half. HCl appeared to be the preferable acid. Figure 1 represents a typical curve used to determine color yields in a series of the tabulated samples, and Tabulation 1 presents the readings upon which these standard curves were based. The actual figures for reporting dye yields in micromoles/liter were computed from the formula c = D/K, K being a weighted value from actual determinations of D from the [illegible] of known dye concentrations under the stated conditions. Weighted value of K for the region of dye values of importance = Summation D/Summation c.

Assumed values of K:

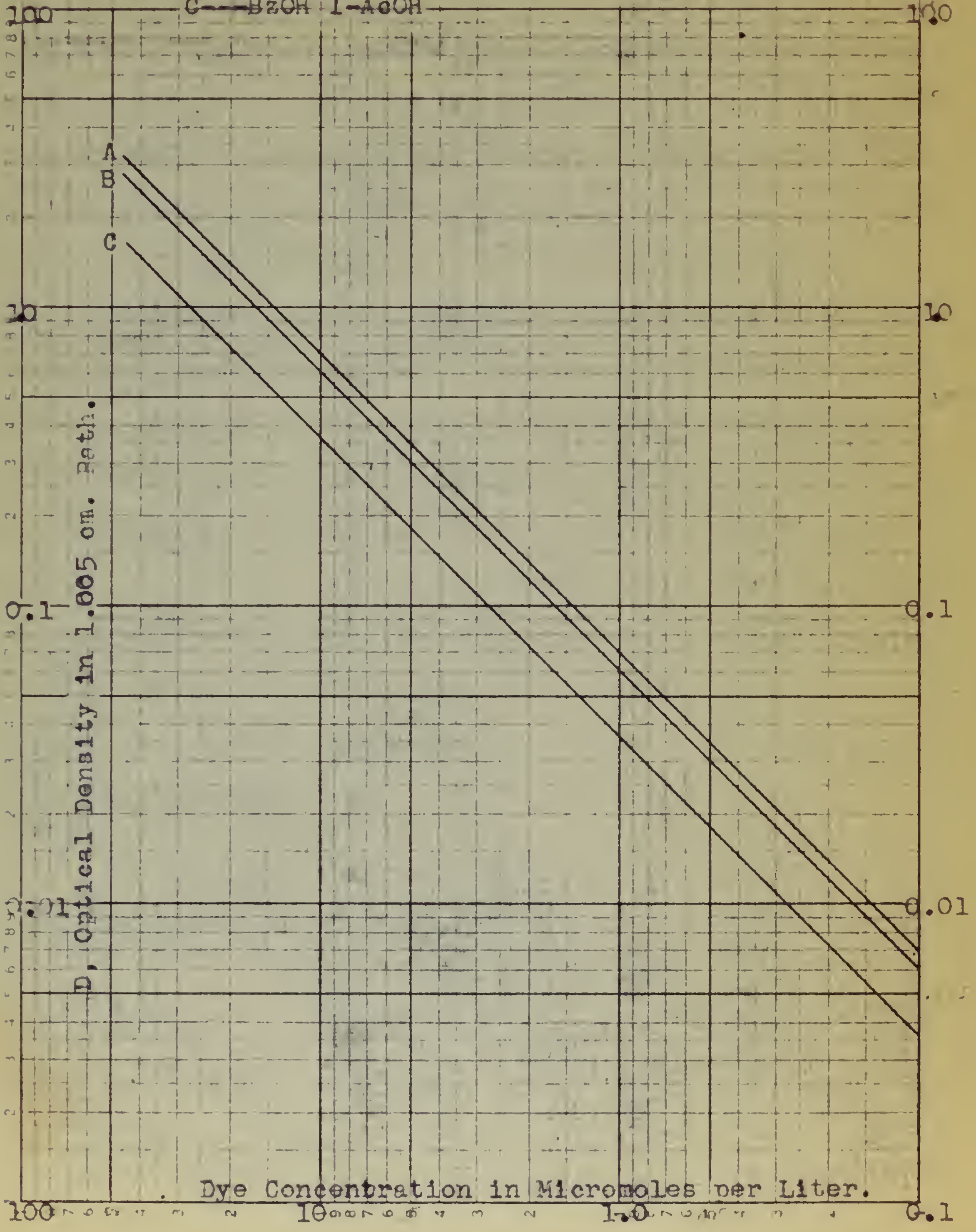
Solvent	Acid Content drops/5cc	K
Benzyl Alcohol	1 of AcOH	0.0397
Benzyl Alcohol	5 of AcOH	0.0700
Benzyl Alcohol	5 of 0.04N-HCl	0.0700
Acetone	5 of 0.04N-HCl	0.0799
Acetoacetic ester	5 of 0.04N-HCl	0.0513

AcOH = Glacial Acetic Acid

Figure I

Typical Color Standard Curves
Optical Density in 1.005 cm. at 6400 Angstroms
vs
Concentration of Dye in Micromoles per Liter.
(Assumes 1 mole MG-Oxalate = 2 moles dye.)

A---BzOH 5-AcOH, BzOH 5-HCl, Acet 5-HCl.
B---AAE 5-HCl.
C---BzOH 1-AcOH



When the color standard dilutions were stored in silicone coated containers some fading occurred as compared with the uncoated containers. (Refer to Tabulation I, Summary of E-values). This can be attributed to adsorption of a film of dye on the wall of the container, and its loss from solution. Since controls were kept on all irradiated samples, this effect was automatically accounted for in reading the radiation-caused color changes, using E-values in all instances for the unfaded color standards.

Four of the standard color solutions, containing no acid, in benzyl alcohol, were given an x-ray air dose of 8800 r, at 550 r per minute. No appreciable color change was noted. The possibility of a color destruction due to the irradiative effects on the color was possible, but in a system involving such a number of heterogeneous reactions, it was desired only to record the net color concentration, it being impossible at present to state the degree to which adequately excited leucocyanide molecules fail ultimately to produce a dye molecule.

(5) Controls:

The ideal situation would have been to read each sample spectrophotometrically before and after irradiation. However, due to the fact that prolonged exposure to ordinary room lighting over a period of minutes might tend to accumulate errors in the samples, it was decided instead to

prepare non-irradiated controls of each type of sample irradiated, and to employ them as indicators of the pre-irradiation condition of the other samples. Naturally this introduces a large degree of uncertainty into each measurement, but for a single set of measurements the uncertainty appears to be small. At the time the decision was made, the errors accumulated by exposure to room light of the concentrations used were small but unknown, and insufficient pure chemical was on hand to estimate such variations. In future tests of this nature it is suggested that all samples be stored in pyrex glass vials with a 5 cm. optical path length integral in each vial for the purpose of spectrophotometric interpretation. In this manner, each vial can be read spectrophotometrically as often as desired without disturbing the sample in any manner or exposing it to any stray light. In addition, the sensitivity of the system would be increased approximately 5 times in reading slight color changes, due to the five-fold increase in optical path length.

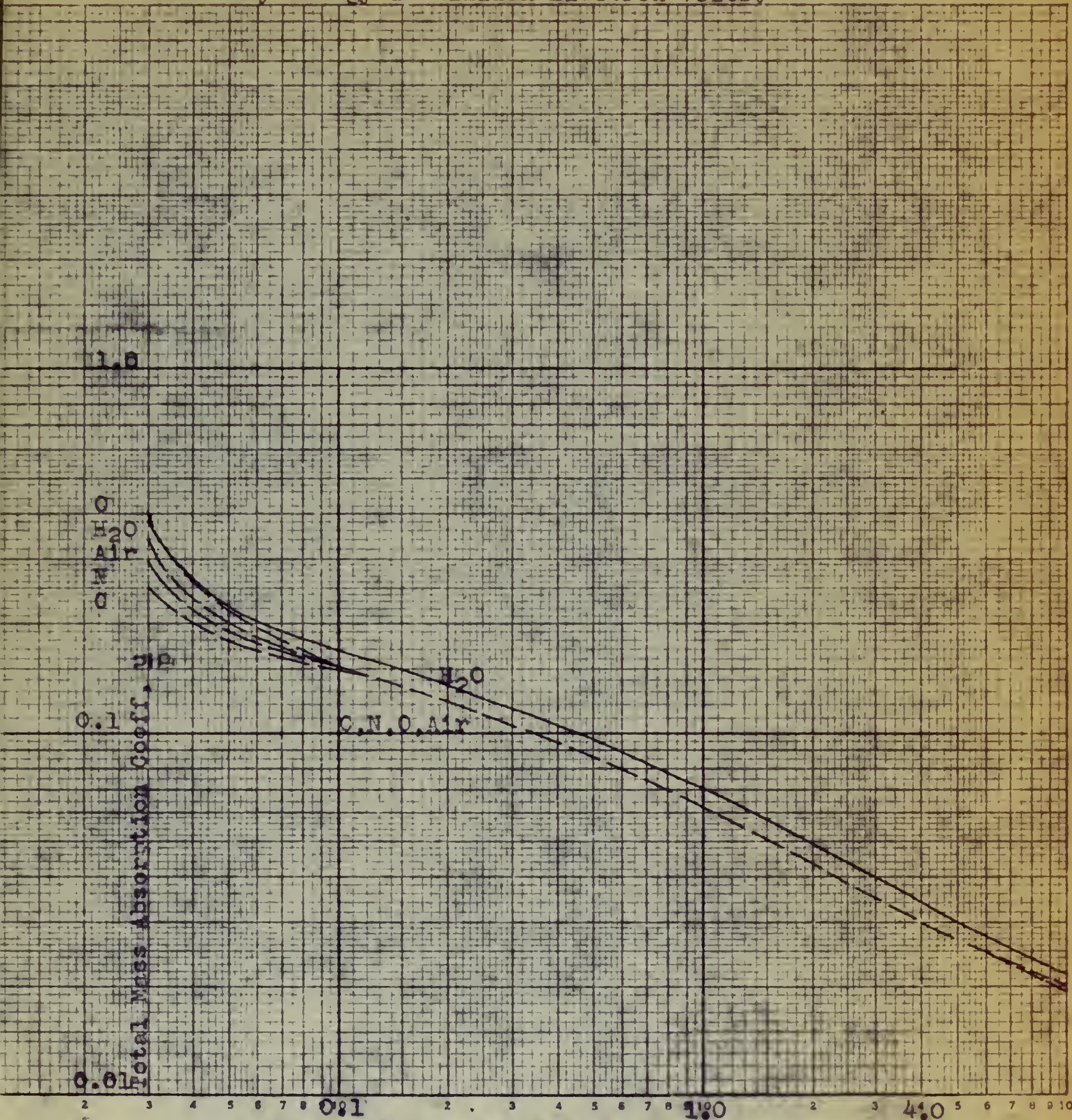
(7) Experimental results:

For purposes of comparison, an artificial adjusted air dose of radiation was computed for each sample, the adjusted dose being computed in terms of the calibrated air dose in Roentgens (r) multiplied by the density in grams per cubic centimeter (d) of the sample. Refer to the graph of total mass absorption coefficients of the elements C, N, O and

Air, Figure II. Assuming the irradiated samples to be thick in nature, since they cannot be treated as infinitely thin samples, one will note that it is reasonable to assume both for the 200 Mev x-rays filtered by the glass sample container and for the 4 Mev gamma rays (plus considerable softer scattered radiation) that the mass absorption coefficients of the elements and air are nearly equal. One can then relate the absorbed radiation energy dissipated in each sample merely to the product of the calibrated air dose and the liquid density of the organic solvents employed. For a more detailed exposition of the reasoning behind this assumption, refer to Lee (L-4). By shielding the air-wall r-meter with a soft glass shell vial similar to those used for all test irradiations, it was found that the shielding effect of the glass wall was equal for both the x-rays and the gamma rays employed. (Refer to X-ray and Gamma Ray Experimentation, Part (2).). In this way it was decided that for comparison purposes the effect of the glass wall could be ignored; for absolute computations, of course, it could not be ignored.

Specific color yields were computed as (sum c/sum 1000rd) = L, the number of micromoles of dye formed per liter per 1000rd, adjusted air dose of radiation.

Total Mass Absorption Coefficients of C, N, O, Air & H_2O
vs
Gamma Ray Energy in Million Electron Volts.



Gamma Ray Energy in Mev.
(Private Communication, Major N.M.Lulejian, USAF.)

A. 4 Mev Betatron results.
(Refer to Tabulation II - 4 Mev Betatron Tests.)

All samples were irradiated at 45 air r/min in soft glass vials in identical geometry for 90 minutes each, a total air dose of 4050 r, or an adjusted air dose of 4225 rd in Benzyl Alcohol. The following results were noted:

Solvent	C = net dye formed, micromoles per liter	L = net dye per 1000 rd
(a) Benzyl Alcohol, 0.0112 moles/liter leucocyanide, no acid during irrad.	0.92	0.218
(b) Benzyl Alcohol, 0.0112 moles/liter leucocyanide, 5 drops AcOH/5cc.	1.21	0.287
(c) Benzyl Alcohol, 0.0112 moles/liter leucocyanide, 5 drops AcOH/5cc.	1.03	0.244

Sample (c) is sample (a) re-irradiated for a second time. Due to the uncertainty and poor control of geometry and temperature during each 90 minute irradiation, these three results agree within the allowable limits of error, and average to give a specific color yield of 0.25 micromoles per liter per 1000 rd, with a leucocyanide concentration of 0.0112 gram moles per liter.

Solvent	C	L
(d) Acetoacetic Ester 0.014 moles/liter leucocyanide, 5 drops 0.04N-HCl/5cc.	-0.12	-0.029

(the (-) sign denotes decolorization)

B. 200 Kev x-ray results.
(Refer to tabulation III - 200 Kev x-ray results.)

Figure III is a plot of net color yield in Benzyl Alcohol, micromoles of dye per liter vs adjusted air dose (rd) of 200 Kev unfiltered x-rays, administered at the rates of 400 air r per minute and 200 air r per minute, for various concentrations of leucocyanide in solution in gram moles per liter in glass walled containers.

Figure IV is a similar plot for a limited number of acetone solutions, and includes two points for the radiochemical production of dye from the dye leucobase (easily oxidized to the dye, but not photosensitive to ultraviolet light), and also a comparison with a benzyl alcohol solution of similar leucocyanide concentration.

In Figure V is plotted the specific color yield, micromoles of dye per liter per 1000 rd adjusted air dose, against the concentration of leucocyanide in solution in gram moles per liter in benzyl alcohol, acetone and acetoacetic ester, contained in both soft glass wall and silicone coated containers.

The deliberate variation in x-ray dose-rate from 400 r to 200 r per minute was unfortunate in that, in altering the geometry to halve the dose rate, the wooden platform upon which the samples were supported was not also moved back from the x-ray source with the samples, and as a result a large undetermined amount of secondary scattered radiation was introduced. Theory predicts that, if the

yield is dependent on dose-rate, the yield should decrease with reduced dose rate. The results, when the betatron was used with a dose-rate one-tenth that of the x-rays, indicate that the leucocyanide system in benzyl alcohol is not critically dependent on dose-rate.

The x-ray curves show an increased yield with the decreased dose-rate of x-rays out of all proportion with the possible variation any theory allows, and thus this anomalous result can best be explained by the secondary scattered radiation introduced in the experiment.

Due to the fact that experimental variations inherent in these chemical systems are rather large for each single sample, (± 20%), the discussion of the experimental results, and the conclusions drawn, will be based on the trend of the curves in Figures III, IV, V, rather than upon the individual experimental points themselves.

Figure III

Net Dye Yield in Micromoles per Liter
of Benzyl Alcohol
vs
Adjusted Air Dose in 1000 rd of 200 Kev X-rays
and 4 Mev Gamma Rays. (Multiply by 0.8 to
obtain approx. solution Radiation Dose in r.)
BzOH-Benzyl Alcohol.
MGCN-Malachite Green Leucocyanide.

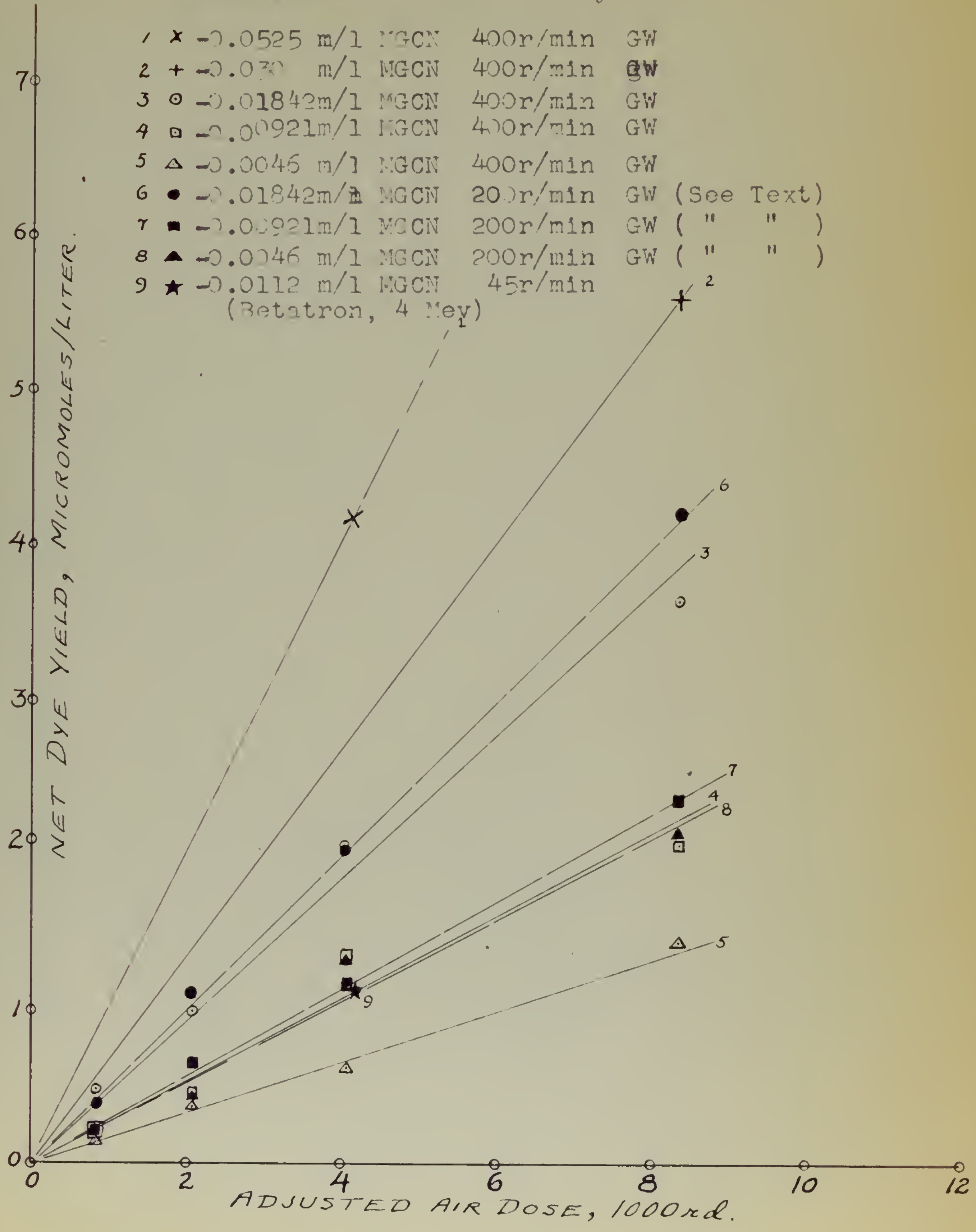


Figure IV

Net Dye Yield in Micromoles per Liter
vs
Adjusted Air Dose in 1000rd of 200 Kev X-rays
(Multiply by 0.8 to obtain approx. Solution
Radiation Dose in r.)

BzOH-Benzyl Alcohol
Acet-Acetone
MGCN-Malachite Green Leucocyanide
MGH -Malachite Green Leucobase

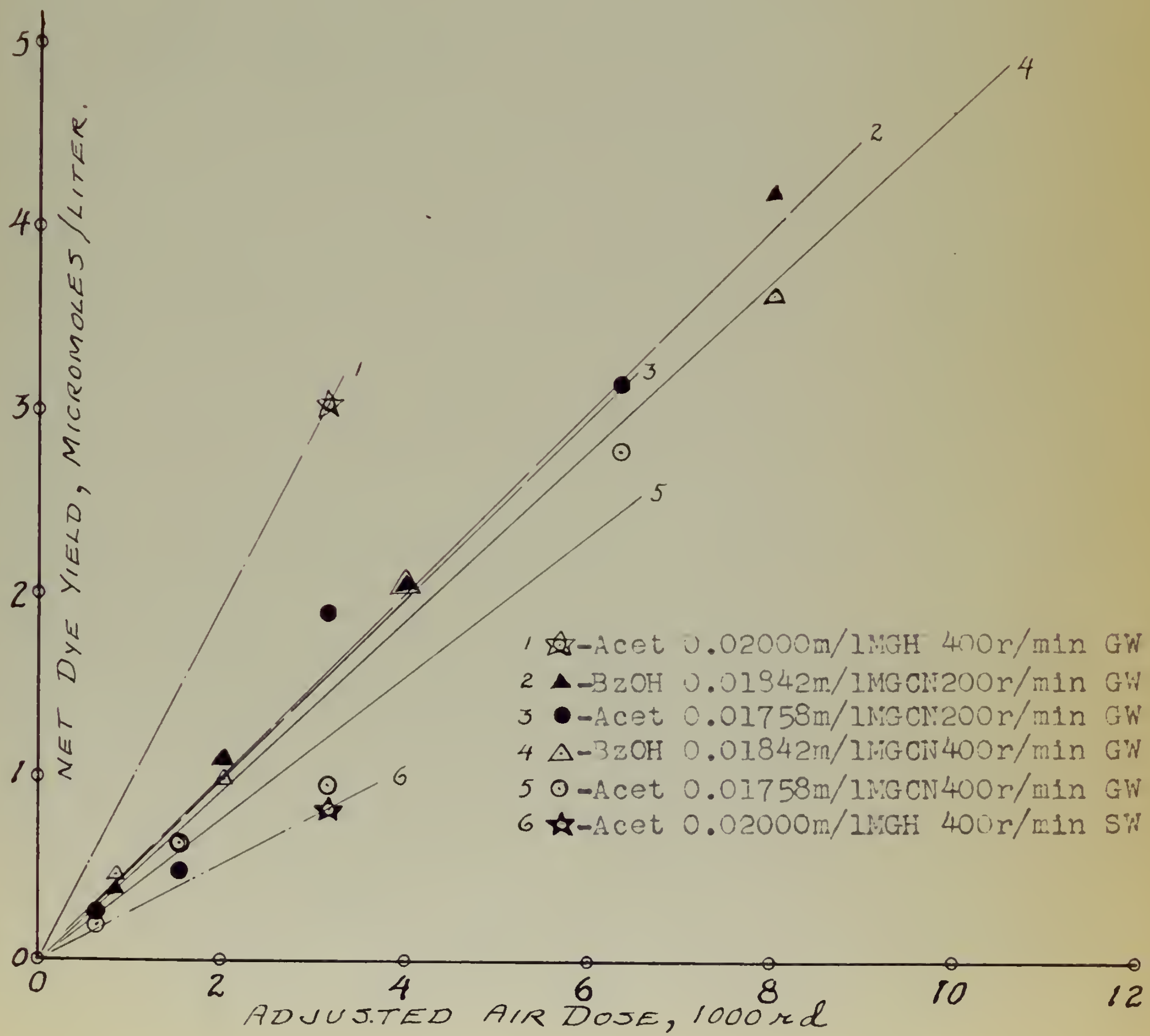
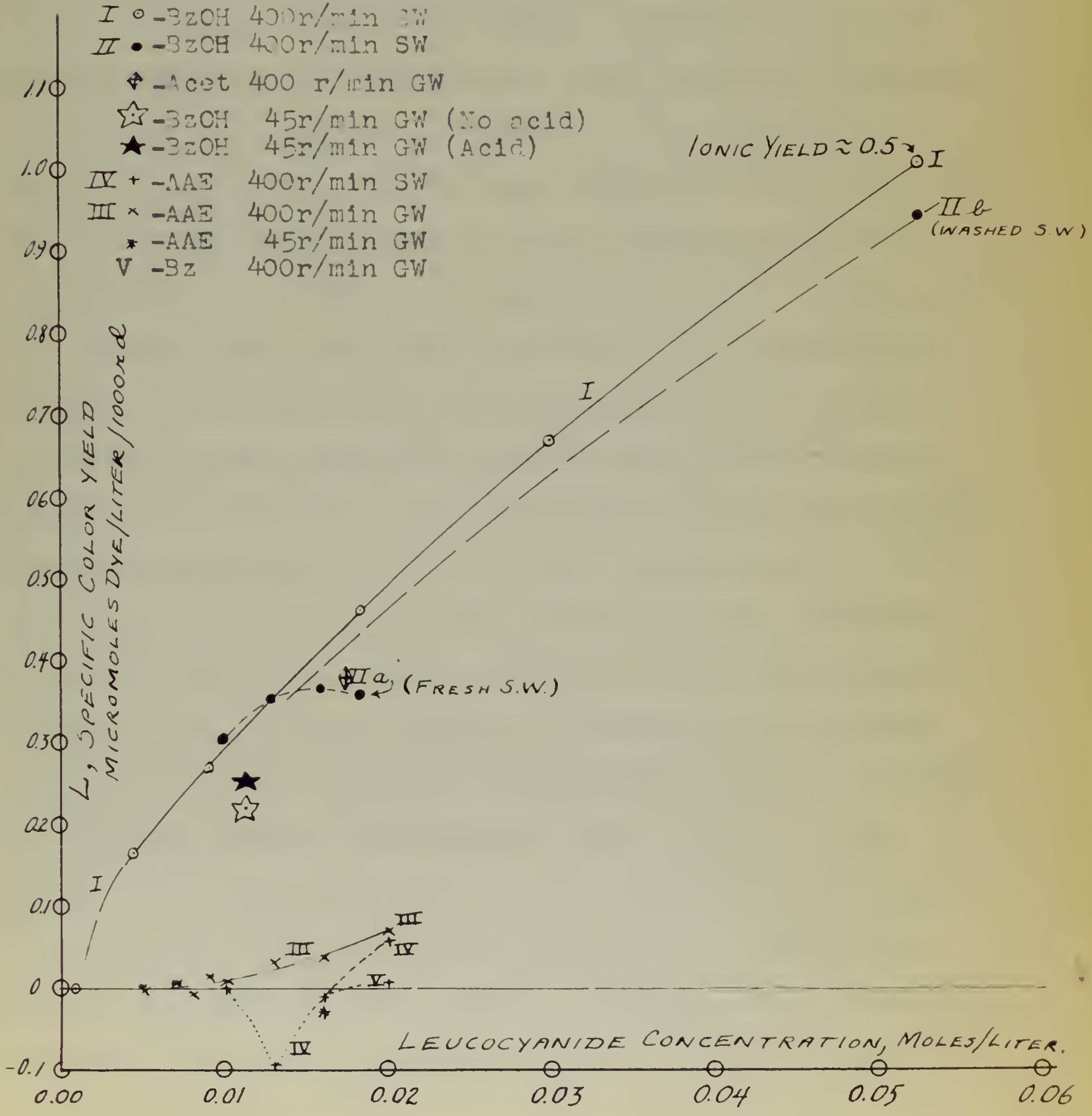


Figure V

Specific Dye Yield in Micromoles per Liter per 1000rd
vs
Malachite Green Leucocyanide Concentration in Moles/Liter.
200 Mev X-rays and 4 Mev Gamma Rays (Betatron).



Discussion and Conclusions

A. Theory

As in many photolytic reactions that are well known (R-1), one can not state that a quantum of energy is absorbed by a single chemical bond in a molecular structure. The light absorption characteristics of a given molecular structure are determined in many portions of the absorption band spectra by the bond structure of that molecule, but upon absorption of a quantum, the entire molecular system is excited, not just the particular bond providing the capability of that quantum being absorbed. Absorption of an exciting quantum anywhere in the molecule will quite often cause the rupture of a particular bond or bonds. Acetone vapor, when irradiated by light of 2537 Angstroms, breaks down to form methyl radicals and CO, the methyl radicals largely recombining at room temperature to form the original acetone, but at elevated temperatures to form ethane, methane and CO (R-4); when slightly aqueous, the yield contains some CO_2, more methane, CO, and traces of AcOH in addition to ethane. Two bonds are broken simultaneously by a single quantum. A similar single quantum double bond rupture occurs in acetoacetic ester to produce CO, methyl radicals and CH_2CO_2Et (R-5) at 2850 A. No ultraviolet decomposition of benzyl alcohol was found by Berthelot and Gaudechon (R-6), although the solvent is highly absorbing in that region. However, due to the stability of the aromatic nucleus on this alcohol, it is

probable that the absorbed energy is dissipated by that stable structure before dissociation can occur. In the cases where a straight chain is attached to an aromatic nucleus, the straight chain is attacked by light energy absorbed anywhere in the energy structure of the molecule. Both benzyl alcohol and acetone fluoresce highly when irradiated with ultraviolet light, (B-4)(B-5)(C-3), an appreciable portion of the fluorescence being in the near ultraviolet. Little fluorescence of acetoacetic ester, acetic acid and methyl alcohol is observed under similar conditions, since the type of ultraviolet excitation is not similar - these three solvents do not demonstrate an absorption band in this ultraviolet region, but only continuous absorption. In Figure VI - A are seen the plots of the relative absorption characteristics of these solvents. In Figure VI-B are similarly plotted the information for solutions of malachite green dye, leucocyanide, and carbinol. The data for the leucobase was not available.

When one of the above solvents, (benzyl alcohol, acetone, acetoacetic ester, acetone and methyl alcohol) is irradiated with x-rays or gamma rays individually in the pure state, it is reasonable to assume that in the process of decomposition of the solvent by the highly ionizing effects of the absorbed radiation, many of the excitation states *characterized by the light energy absorption spectra* are simultaneously created in the solvent molecules and also the decomposition products. One may also assume that if the

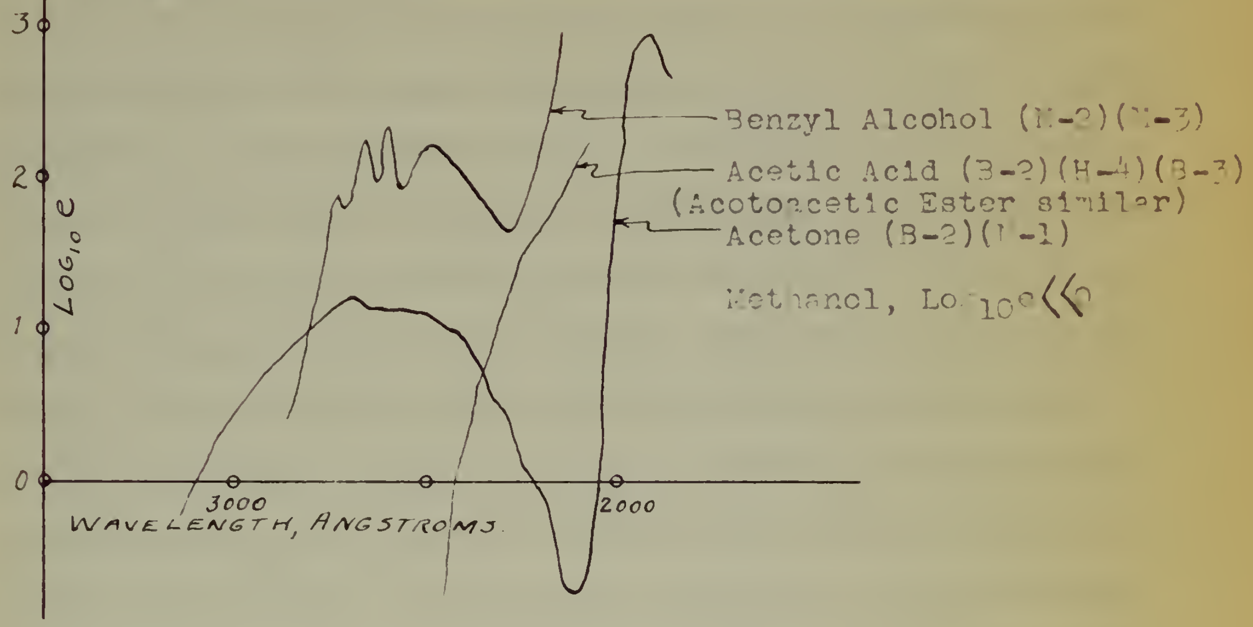
molecular structures under consideration do not exhibit absorption spectrum bands at particular energies, then these particular energy states will not be greatly excited in the solvent. If the above is true, one would expect to observe fluorescence excited in the pure solvents by the absorbed x- or gamma radiation similar to that actually observed from ultraviolet excitation. Such is not the case to any marked degree. However, the sensitive measurements made by Kallmann (K-1)(K-2) do demonstrate a small amount of fluorescence in all common solvents, irradiated with gamma rays, which was characteristic of each of the solvents, and his experimental results upon addition of small amounts of fluorescent impurities to the solvents irradiated with gamma rays prove a high degree of excited states in the solvents due to the absorbed radiation. Whether the energy excess is that of the parent solvent molecules or that of the solvent decomposition products cannot be readily determined at this time from the available data; however, Kallmann strongly urges the adoption of the view that semi-stable exalted states are created in the solvent molecules, with subsequent resonance transference through a chain of solvent molecules to the fluorescent impurity.

The structure of malachite green leucocyanide is quite stable chemically, resisting any decomposition when boiled in acidified acetone, methyl alcohol or ethyl acetate for periods of an hour or more. Some decomposition does occur

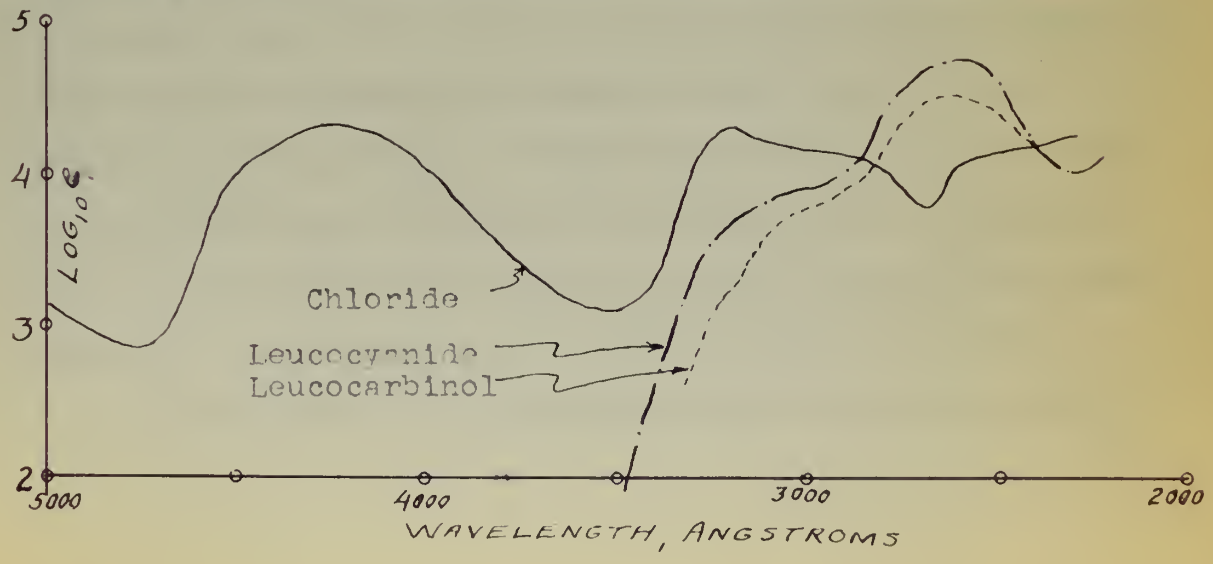
Figure VI

Extinction Coefficient Log$_{10}$e
vs
Light Wavelength in Angstroms, for

A. Acetone, Benzyl Alcohol, Acetic Acid, Acetoacetic Acid and Methyl Alcohol.



B. Malachite Green Leucocyanide, Leucocarbinol & Carbinol in Ethyl Alcohol. (H-1)



in aqueous acetone, explained as a water-catalyzed thermal formation of dye and acetone cyanohydrin. However, when the molecule in an ionizing solvent is excited by an absorbed ultraviolet quantum, photolysis to form the dye ion and a cyanide ion always occurs. If the leucocyanide is present in a solvent irradiated with x- or gamma rays, photolysis of a similar kind will occur if the leucocyanide molecule absorbs sufficient energy (3-6ev) from a neighboring excited solvent molecule, ion, radical or electron by collision or resonance energy transference, or due to direct absorption of an initial x- or gamma ray photon. Since the dye ion, when once formed in an ionizing solvent capable of sufficient association with the cyanide ion to prevent its immediate recombination with the dye to reform the leucocyanide molecule, is remarkably stable, the process of permanent color formation appears quite probable, and is found to be so in both benzyl alcohol and acetone. Color is formed to a much lesser degree in ethyl acetoacetate, and apparently to a very small degree, if at all, in methyl alcohol and acetic acid. Of course, the actual degree of color permanently formed depends on the leucocyanide concentration, the response of the solvent to the absorbed irradiation, and the rates at which the excited solvent molecules and decomposition products lose the ability to excite leucocyanide photolysis by self-quenching, recombination and other chemical processes.

A comparison of the degree of color formation from

leucocyanide with the ability of the solvent to maintain an excited state in the energy region capable of altering the leucocyanide molecule should be considered. Benzyl alcohol and acetone give practically identical results, within the limits of the experiment (Figure V); both of these solvents are highly excitable in the proper energy region, as shown by the ultraviolet absorption band spectra, and both fluoresce in an energy region (2800Å - 3200Å) capable of properly exciting leucocyanide molecules. Acetoacetic ester, at identical concentrations of leucocyanide, produces little color (one-seventh or less) under identical conditions of irradiation; this solvent has only continuous ultraviolet absorption in the proper region. Methyl alcohol has only a slight continuous ultraviolet absorption and failed to produce measureable color; acetic acid, again with only continuous absorption and no band spectra throughout the ultraviolet region of 4500 to 2000 Angstroms, failed to produce a colored dye typical of malachite green when x-irradiated.

In all of the above solvents, ultraviolet absorption by the leucocyanide produced a rapid photolysis to a stable color typical of malachite green.

That the photolytic effect produced in the leucocyanide molecules in very dilute solutions, by x-rays and gamma rays, is an indirect effect is evident from several facts:

(a) The x-ray and gamma ray absorption effect is very

dependent upon the solvents employed, whereas each solvent acts identically when the colored ion is produced by direct absorption of U-V quanta in the leucocyanide molecules. If the color were being produced only by direct hits of initial x-ray or gamma ray photons in the leucocyanide molecules, there should be little or no solvent dependence.

(b) Later, a rough computation of the ionic yield will be attempted. When 0.0525 gram moles of leucocyanide are dissolved in one liter of benzyl alcohol (the maximum concentration studied), there are 18.6 grams of leucocyanide dissolved in 1043 grams of solvent. Since both solvent and solute are practically identical in x-ray absorption, the energy dissipated in the leucocyanide molecules is only 2% of the total energy dissipated in the solution. An air dose of 4000 Roentgens is estimated to result in an actual dose in the solvent (due to the shielding of the glass container, etc.) of about 3200 Roentgens. According to Lea (L-4), 1000 r is equivalent to 5.24×10^{16} electron volts per gram of air. Roughly, then 3200r is equivalent to 1.75×10^{20} electron volts per liter of benzyl alcohol. Under these conditions, it was found that 4.21 micromoles of dye per liter were produced by the irradiation, equivalent to the specific alteration 2.53×10^{18} molecules of leucocyanide per liter of solvent.

Therefore, if one assumes direct hits on only leucocyanide molecules to be effective, 2% of the total absorbed energy will be effective, or $0.02 \times 1.75 \times 10^{20} = 3.5 \times 10^{18}$

electron volts per 2.56 x 10^{18} molecules of leucocyanide altered to form dye, or about 1.4 electron volts per molecule altered! Since in a 200 Kev continuous x-ray spectrum the majority of the photons have an energy of about 100,000 electron volts, each x-ray photon absorbed would have to alter at least 7000 leucocyanide molecules before being absorbed, losing a uniform amount of energy of only 1.4 ev per molecule before being completely dissipated. This is insufficient energy to cause photolysis of a leucocyanide molecule.

Therefore, one may safely assume that the effect produced is a typical indirect effect as described by Lea and Glasser. The above computation then permits approximately 70 electron volts to be dissipated in the benzyl alcohol for each leucocyanide molecule specifically altered to produce a dye molecule as recorded spectrophotometrically, when 0.0595 gram moles of leucocyanide are dissolved in one liter of benzyl alcohol. This is a very reasonable figure for such a system. There is absolutely no evidence that a chain reaction could be involved in the process, since the ultraviolet quantum yield studies indicate no temperature dependence, nor do they indicate a quantum yield in excess of unity even for very energetic quanta (H-3).

As was true in the case of ultraviolet photolysis, no dye was produced from the leucocyanide in benzene by x-rays (Figure V, plot V). This proves the requirement that certain

types of ionized solvents are required for photolysis.

B. Wall effects.

In the usual heterogeneous chemical reaction, such as that produced by absorbed x-rays or gamma rays in a solvent, it is always advisable to study wall effects, especially where the wall area of the containing vessel is large in proportion to the volume of the vessel, and where the dilution of the substance being studied is rather large (R-1). Since in a liquid the molecules are always in constant collision with each other and the vessel walls, the possibility of energy loss by quenching and chemical combinations at the wall is sometimes high. In cases cited by Rollefson, reactions assumed to be occurring in the volume of the sample were actually occurring only in the film adsorbed on the container wall.

It is possible to alter the wall characteristics of a glass vessel without altering the radiation geometry or absorption characteristics of the system by coating the glass wall with a silicone coat, ('Dri-Film', Appendix C (c).) If in the subsequent radiation-caused reactions quantitative yield is dependent upon the nature of the wall surface, one may then assume that the observed yield is the net result of a heterogeneous series of chemical reactions in the container. If independent of the wall surface, a homogeneous reaction yield is suggested.

A soft glass container acts as a wall somewhat basic in character. A "Dri-Film" wall is made up of methyl groups, and acts as a very stable saturated hydrocarbon in the surface chemistry. It was noted previously that color standards in silicone coated containers tended to fade in the liquid portion even though acidified, and was reasonably explained as an adsorption of the dye on the silicone coating (Tabulation I - Color Standards). Referring to Figure V, plots I and II, it is noted that the difference of the two benzyl alcohol-leucocyanide dye specific yield curves is small, and irregular. Here one may assume that the deviation of the two plots is probably simply due to a leaching of dye from solution by the fresh silicone wall coating (especially in IIa). If a small dependence on wall nature is present during irradiation, it is probable that the excited dye molecules, especially in the larger concentrations, tend to adhere more readily to the silicone wall than when stabilized without irradiation, as in the color standards.

In Figure V, plots III and IV, the same effect is noted for leucocyanide color production in irradiated acetoacetic ester as in benzyl alcohol. Here, however, the specific color yield is so low initially in the glass-walled container that the observed yield in the silicone walled container appears at the best to be a decolorization process for the leucocyanide concentrations studied.

Combining the above observed effects with the comparison

in Figure VI of the effect of x-ray dosage at 400 r/min. in contrast with gamma ray dosage at 45 r/min. for the specific color yield from leucocyanide in both benzyl alcohol and acetoacetic ester, one observes that the benzyl alcohol yield is relatively independent of dose rate, while the acetoacetic ester yield is strongly dependent upon dose rate, the specific color yield actually being negative (decolorization) at the lower dose rate. According to Lea (L-4), dose rate independence in an indirect action bespeaks a homogenous reaction; heavy dependence on dose rate indicates a largely heterogeneous reaction.

The results seem to indicate a practically homogenous efficient reaction to produce color from the leucocyanide in benzyl alcohol, and a very heterogeneous inefficient color-producing reaction in acetoacetic ester. It appears, therefore, that the color production initially may be due to two different mechanisms in the two solvents.

In order further to investigate the nature of the wall reaction in the soft glass and silicone coated vials, a series of irradiations were made of malachite green leucobase, 0.02 gram moles per liter of solvent at 4000 r air dose and 400 r/min. in acidified benzyl alcohol, acetone, and acetoacetic ester (Tabulation III - x-ray results, Series III). The specific color yield of the leucobase was not generally similar to that of the leucocyanide. In both benzyl alcohol and acetone, the specific yield in the glass wall was four

times that in the silicone wall. It can be argued that the color producing mechanisms in this case in acetone and benzyl alcohol are somewhat similar, and are strongly quenched by the silicone wall. No quantitative comparisons other than this can be made, since acetone, when acidified with aqueous acid tends to react thermally with the leucobase and to destroy the color initially produced, especially in the silicone coated containers. The leucobase is relatively stable in benzyl alcohol, but in acetoacetic ester slowly oxidizes to form the dye. When irradiated in acetoacetic ester, the specific color yield from the leucobase was found to be similar to that in benzyl alcohol, and was greater in the silicone coated container than in the glass one. It is apparent that the leucobase-solvent system under identical conditions of irradiation is somewhat similar to the leucocyanide-solvent system in sensitivity, but, as revealed by the anomalous dependency on wall effect, the causative mechanisms of color production are not the same. It is quite probable that the production of color from the leucobase in these solvents is heavily dependent upon the per cent of water, pH, and oxygen content of the solvent, since this dependency is typical of its chemical nature under ordinary conditions (C-2).

C. Ionic yield.

Since, due to the lack of enough pure leucocyanide, it was not possible to follow the specific color yield

leucocyanide concentration plot to a point where a maximum color yield independent of increasing concentration (L-4, p.43) becomes apparent in benzyl alcohol (or to the limitation imposed by the saturated solution), the maximum ionic yield cannot be estimated. However, referring to Figure V, plot I, the highest experimental point on this curve will be chosen for a sample estimate:

Leucocyanide concentration = 0.0525 moles/liter

Density of benzyl alcohol = 1043 grams/liter.

Specific Color Yield = 1.018 micromoles/liter/1000rd.
(Tabulation III, Series III-0)

N = Avogadro's Number = 6.02×10^{23} molecules/mole.

In Air, 1r = 6.77×10^{10} electron volts per 0.001293 grams of Air
(L-4,p.7)

1000r = 6.77×10^{13} ev/0.001293 gm. air
= 5.24×10^{16} ev/gm. of air

Assuming that 1000r dissipates the same energy per gram of benzyl alcohol as it does per gram of air,

1000r = 5.47×10^{19} ev per liter of benzyl alcohol.

It is necessary to assume (checked approximately by several measurements with the air wall r-meter) that 1000r air dose of x-rays (1043 rd adjusted dose for benzyl alcohol) is an actual dose of 800 r absorbed in the solvent as shielded by the glass-walled container.

Thus, 1000r air dose = 4.37×10^{19} ev per liter BzOH.

1.043 L = Specific dye yield/1043rd = specific dye yield /1000r air.

1.043L = 1.043 x 1.010 = 1.05 micromoles dye formed per liter BzOH per 800r.

Yield = 6.32 x 10^{17} dye molecules formed per liter BzOH per 800r.

Average energy dissipation per molecule of dye formed:

= 437.0/6.32 = 69 ev/molecule of dye formed.

Although no information is available concerning determinations of the average amount of energy expended in benzyl alcohol per ion-pair produced by x- or gamma radiation absorbed in the solvent, it is reasonable to state that the 69 ev dissipated per dye molecule formation corresponds roughly to an ionic yield of slightly less than 0.5.

D. Dosimetry

Insufficient data are available to permit an estimate of the maximum sensitivity of the system, malachite green leucocyanide in acidified benzyl alcohol, as a dosimeter for x-rays, gamma rays, and other ionizing radiations, especially at very low dose rates. If the maximum ionic yield were found to be in the neighborhood of 1.0, one could expect a color formation of about 2 micromoles of dye per liter per 1000 roentgens, solution dose. Allowing for a reasonable amount of variation (± 10%), one would expect to find spectrophotometric interpretation possible at 6400 Angstroms of total solution doses of 100r minimum to 20,000r maximum in a 1 cm. optical path length, or 25 - 4000r in a 5 cm. optical path length. If the solution were anaerobically sealed in pyrex glass standard containers with an

integral optical path, capable of insertion in a standard photoelectric colorimeter, it is possible that a rather stable system for lower dose rates could be developed. In a disposable container of that type excellent autoindicating dose rate and disintegration studies of a radioactive beta or gamma emitter in solution in the dosimetric solution itself are possible.

The most ideal features of a color-producing chemical dosimeter of this type are that the solution may be permanently sealed before irradiation, the color needs no additional chemical development after formation for interpretation, color readings may be made accurately and conveniently in a relatively inexpensive photoelectric colorimeter at any time and as many times as desired, and lastly the system does not appear to depend upon a thermal chain reaction for the production of the color. Being in liquid form, the dosimetric solution may be contained in any shape or volume convenient for the nature of the experiment. It is to be hoped that extension of these preliminary results indicate dosimetric possibilities. It is not suggested that visual colorimetric interpretation of the color formed be recommended, because of the known physiological limitations in the human eye in quantitatively judging color density and quality.

E. Summary.

Of the three solvents, acetone, acetoacetic ester and benzyl alcohol, only benzyl alcohol has ever been irradiated

by x-, gamma, beta or alpha radiation and the results reported. Kailen in 1932 (K-3) exposed pure benzyl alcohol aerobically for six months to the beta and gamma rays of 0.11 grams of radium, and found at the end of that time that a large quantity of monobasic acid was produced. Specific Conductivity in the irradiated sample was 150 times that of a non-irradiated control. The acid produced was measured by titration as monobasic acid. His computations follow:

m = no. of molecules of monobasic acid formed per second in the irradiated liquid more than the number in the liquid not irradiated.

n = no. of ion-pairs formed per second by absorption of the beta and gamma rays.

Experimental Results (K-3) Computed:

	m	n	m/n
Pure Benzyl Alcohol	$8.5x10^{13}$	$5.0x10^{13}$	1.7
Pure Benzyl Alcohol in Benzene	$3.8x10^{13}$	$4.7x10^{13}$	0.82

These computed results are undoubtedly in error, since Kailen assumed that, in computing the ion pairs produced, the specific ionization of beta and gamma rays is the same as that of alpha rays, assumed in benzyl alcohol to be that of benzene, 1.29 (footnote). It is evident, therefore, that his figure given for "n" is much too large, that "m/n" is much greater than reported, and that a chain reaction is occurring, catalysed by the absorbed radiation; this is to be expected, due to the autooxidative nature of benzyl alcohol.

Kailen's results, although erroneous, do suggest that practically all of the absorbed radiation in aerobic benzyl

alcohol is expended in exciting the auto-oxidation of the solvent. Since, as computed in part C, Ionic Yield, leucocyanide photolysis is also capable of accounting for a large portion of the absorbed energy, probably the leucocyanide acts as a protective agent in benzyl alcohol, draining off the excess energy from the activated solvent before permanent alteration of the solvent molecules occurs. A more detailed investigation is required, however, before the nature of the process is capable of interpretation.

Footnote: Quote: "Ferner wurde die spezifische Ionisation der beta und der gamma-Strahlen ebenso gross wie die der alpha-Strahlen angenommen ..... Unquote. (F-3)

Suggestions for Future Work:

Since a rapid and simple method of preparing large quantities of pure leucocyanides of triphenylmethane dyes has been developed (Appendix A), it is possible to suggest several avenues of future work:

(a) Similar studies of the leucocyanides and of other of the triphenylmethane dyes.

(b) The preparation and irradiation of benzyl alcohol solutions of malachite green leucocyanide of high concentration in order that the curve of specific color yield as related to leucocyanide concentration may be fully known (Figure V), in order to estimate the maximum ionic yield possible.

(c) The investigation of the relative effects of gamma and x-rays, beta and alpha particles, neutrons and positrons upon sensitive leucocyanide solutions under varying conditions of temperature, oxygen tension, dose rate, and type of solvent.

(d) With the above knowledge, the development of accurate dosimetric solutions and gels capable of colorimetric interpretation.

(e) An investigation of sufficient theoretical depth to develop a theory adequate to explain the nature of the energy transfer process from the solvent to the dissolved leucocyanide molecules.

Tabulations I, II, III.

Glossary of Abbreviations:

S = BzOH Benzyl Alcohol
AAE Acetoacetic Ester
Acet Acetone
5-AcOH 5 drops per 5 cc. Glacial Acetic Acid.
5-HCl 5 drops per 5 cc 0.04 N HCl.
GW Soft Glass Wall Container.
SW Silicone 'Dri-Film' coated Containers.

MGCN Malachite Green Leucocyanide in gram moles per liter.
MGH Malachite Green Leucobase in gram moles per liter.
c = dye concentration in micromoles per liter.
(1 mole malachite green oxalate is 2 moles of dye).
%T = % Transmissivity at 6400 Angstroms, 1.005 cm. optical path, compared to doubly distilled water.
Adj. % T = % Transmissivity assuming %T = 100.0 at c = 0.00

D = Optical Density.

K = (Sum D / sum c) from c = 0.10 to 40.0, a weighted constant according to Beer's Law.

L = (sum net c / sum 1000rd), specific dye yield in micromoles per liter per 1000rd.

r/min = calibrated air dose in Roentgens per minute.

r = Total calibrated air dose.

rd = Adjusted air dose, r x d.

d = Solvent density in grams per cm^3.

T = Temperature in ° C.

Age = Number of hours elapsed between mixing and spectrophotometric reading.

Tab I

Tabulation I- Color Standards , % T at 6400 Angstroms.

S	c	% T	Adj. % T	D	K
BzOH	0.000	96.2	100.0	0.0	
1AcOH	0.010	97.0	100.9	- .004	
GW	0.032	96.0	99.8	.001	
Age24	0.100	95.9	99.7	.001	
	0.316	93.4	97.2	.013	
	1.000	85.0	88.4	.054	
	3.162	72.2	75.1	.124	
	10.000	42.6	44.3	.354	
	31.62	6.8	7.07	1.150	0.0367
	100.0	0.3	0.3	2.506	
BzOH	0.00	95.0	100.0	.0	
5-HCl	0.08	94.1	99.1	.004	
GW	0.16	94.1	99.1	.004	
Age5	0.20	94.0	99.0	.005	
	0.40	92.8	97.7	.010	
	0.80	89.1	93.8	.026	
	1.60	83.0	87.4	.059	
	2.00	82.2	86.6	.063	
	4.00	63.8	67.2	.173	
	8.00	21.6	22.7	.644	
	16.00	5.4	5.68	1.245	
	20.00	2.62	2.75	1.561	0.0713
	40.00	0.36	0.38	2.421	
BzOH	0.000	91.6	100.0	.0	
5-HCl	0.066	91.6	100.0	.0	
SW	0.164	88.9	97.1	.013	
Age44	0.410	86.0	93.9	.028	
	1.024	76.9	84.0	.076	
	2.560	58.3	64.0	.193	
	6.40	28.8	31.4	.503	
	16.00	5.58	6.1	1.215	
	40.00	0.26	0.28	2.547	0.0688
AAE	0.000	95.0	100.0	.0	
5-HCl	0.066	94.2	99.2	.004	
SW	0.164	92.1	97.0	.013	
Age44	0.410	89.3	94.0	.027	
	1.024	82.2	86.5	.063	
	2.560	66.3	69.8	.156	
	6.40	42.8	45.1	.346	
	16.00	15.3	16.1	.793	
	40.00	0.90	0.95	2.024	0.0514

S	c	% T	Adj. % T	D	K
BzOH	0.000	94.0	100.0	.0	
5AcOH	0.010	93.2	99.1	.004	
GW	0.032	91.7	97.5	.011	
Age170	0.100	91.4	97.2	.012	
	0.316	86.3	91.8	.037	
	1.000	72.2	76.8	.115	
	3.162	52.0	55.3	.257	
	10.000	18.69	19.9	.702	
	31.62	0.70	0.74	2.128	0.0704
	100.0	0.19	0.20	2.695	
Acet	0.00	96.0	100.0	.0	
5-HCl	0.08	94.8	98.8	.005	
GW	0.16	93.6	97.5	.011	
Age 5	0.20	92.7	96.6	.015	
	0.40	90.2	94.0	.027	
	0.80	84.8	88.4	.054	
	1.60	75.6	78.8	.103	
	2.00	70.8	73.7	.132	
	4.00	52.3	54.5	.264	
	8.00	28.0	29.2	.535	
	16.00	7.7	8.0	1.097	
	20.00	3.8	3.9	1.409	0.0686
	40.00	0.3	0.3	2.468	
AAE	0.000	94.0	100.0	.0	
5-HCl	0.066	94.0	100.0	.0	
GW	0.164	92.2	98.1	.009	
Age44	0.410	89.3	95.0	.022	
	1.024	80.8	86.0	.066	
	2.560	63.4	67.4	.171	
	6.40	36.8	39.1	.407	
	16.00	7.57	8.05	1.094	
	40.00	0.48	0.51	2.292	0.0610

Table II

Tabulation II - 4 Mev Betatron Tests.

No.	S	r/min	r	rd	% T	Adj. % T	D	C	L	
B-0	BzOH 5-AcOH	0	0	0	90.9	100.0	.0	.0	0.00	
B-C	BzOH,0.0112MGCN 5-AcOH	0	0	0	71.6	78.7	.104	1.49	0.00	
B-1	BzOH,0.0112MGCN 0-AcOH	45	4050	4225	61.7	67.8	.169	2.41	0.22	(Acid added after irrad.
B-2	BzOH,0.0112MGCN 5-AcOH	45	4050	4225	58.8	64.7	.189	2.70	0.29	Acid added before irrad.
B-1-A	Reirradiation of B-1.	45	8100	8450	51.6	57.4	.241	3.44	0.23	
								K = 0.0700		
10-0-2	AAE,5-HCl GW	0	0	0	93.0	100.0	.0	.0	0.00	
10-V-2	AAE,0.016MGCN 5-HCl GW	0	0	0	72.0	77.4	.111	1.82	0.00	
10-X-2	AAE " ""	45	4050	4150	73.2	78.7	.104	1.70	-0.03	
								K = 0.0610		

All tests were made as explained in Part (2) of X-ray and Gamma Ray Experimentation.

An initial series of tests were run using very impure malachite green leucocyanide in benzyl alcohol. Before accurate readings could be taken, the color had badly faded in the presence of acid, indicating free cyanide impurities.

An earlier series of qualitative tests showed thatless color than was measurable was formed in absolute methanol when 0.003 gram moles per liter of leucocyanide was in solution, with an air dose as great as 5000 r.

Similarly, even with more than 0.02 moles per liter of leucocyanide in solution in glacial acetic acid, 9900 r air dose failed to produce color typical of malachite green. A brown color was formed, but it was not that of malachite green.

A third series of tests, with glacial acetic acid as the solvent, 9900 r air dose, demonstrated that X-irradiation slightly accelerated the typical oxidation of diphenylamine to a pink dye-- when mixed with leucocyanide, the oxidation was catalysed without irradiation and was tremendously catalysed with irradiation. This appeared in this case to demonstrate the efficacy of malachite green leucocyanide as an active participant in the photodynamic process (G-1, p.1145).

In the following tests, sample color fading in benzyl alcohol was not appreciable over a period of one week after irradiation.

Tabulation III - 200 Kev X-ray Results.

Series I 4-14-51 T 25°C GW K = 0.0700

L-1 BzOH 5-HCl MGCN 0.01842 m/l
E-1 BzOH 5-HCl MGCN 0.00921 m/l
N-1 BzCH 5-HCl MGCN 0.00460 m/l
O-1 Acet 5-HCl MGCN 0.01758 m/l
U-1 BzCH 5-HCl MGCN 0.03000 m/l
V-1 BzOH 5-HCL

(Note- Runs 5 to 8, undetermined amount of extra scatter in excess of 10% inadvertently introduced in geometry.)

Series II 4-24-51 T 25°C K = 0.0700 BzOH 5-HCl
0.0610 AAE 5-HCl

Benzene+MGCN irradiated without acid. All irradiated samples received 4000 r air dose, at 400 r/min.

Adjusted air dose rd :

BzOH	4170 rd
AAE	4100 rd
Bz	3515 rd

Series III 5-2-51 T 25°C K = 0.0700 BzOH or Acet 5-HCl
0.0610 AAE 5-HCL

All irradiated samples received 4000 r air dose at 400 r/min.

Adjusted air dose rd :

BzOH	4170 rd
AAE	4100 rd
Acet	3170 rd

Tab III - I

Tabulation III, Series I 200 Kev X-ray tests, % T at 6400 A

No.	S	r/min	rd	% T	Adj. % T	D	c	L	Wall
0-L-1	BzOH 0.01842 GW	0	0	86.0	91.5	.037	0.53		
1		400	835	80.0	85.2	.070	1.00		
2		"	2085	73.6	78.3	.106	1.51	0.463	
3		"	4170	61.9	65.9	.181	2.59		
4		"	8350	48.1	51.2	.291	4.16		
5		200	835	81.0	86.2	.064	0.91		
6		"	2085	72.3	76.9	.114	1.63	0.500	
7		"	4170	62.0	66.0	.180	2.57		
8		"	8350	43.7	46.5	.332	4.74		
0-M-1	BzOH 0.00921 GW	0	0	89.0	94.7	.024	0.34		
1		400	835	86.1	91.6	.038	0.54		
2		"	2085	81.2	86.4	.063	0.90	0.269	
3		"	4170	71.8	76.4	.117	1.67		
4		"	8350	63.7	67.8	.169	2.41		
5		200	835	86.1	91.6	.038	0.54		
6		"	2085	80.2	85.3	.069	0.99	0.284	
7		"	4170	73.8	78.5	.105	1.50		
8		"	8350	60.7	64.6	.190	2.71		
0-N-1	BzOH 0.00460 GW	0	0	89.2	94.9	.023	0.33		
1		400	835	87.0	92.6	.033	0.47		
2		"	2085	83.8	89.2	.049	0.70	0.165	
3		"	4170	80.7	85.9	.066	0.94		
4		"	8350	70.7	75.3	.123	1.76		
5		200	835	86.1	91.6	.038	0.54		
6		"	2085	83.0	88.3	.054	0.77	0.265	
7		"	4170	72.1	76.8	.115	1.64		
8		"	8350	63.1	67.2	.173	2.47		
0-o-1	Acet0.01758 GW	0	0	86.5	90.1	.045	0.64		
1		635	@ 400	84.0	87.5	.058	0.83		
2		1585	"	78.2	81.4	.089	1.27	0.389	
3		3170	"	74.3	77.4	.111	1.59		
4		6340	"	52.8	55.0	.260	3.43		
5		635	@ 200	83.0	86.4	.063	0.90		
6		1585	"	80.0	83.3	.079	1.13	0.495	
7		3170	"	63.8	66.4	.178	2.54		
8		6340	"	52.1	54.3	.265	3.79		
0-U-1	BzOH 0.03 GW	0	0	72.6	77.3	.112	1.60		
10-U-1	"	400	8350	29.4	31.3	.505	7.20	0.671	
0-V-1	BzOH	0	0	94.1	100.0				
10-V-1	BzOH	400	8350	97.9					
	Acet	0	0	96.0					

Tab III - I

Tabulation III, Series I 200 Kev X-ray tests, % T at 6400 A

No.	S	r min	rd	% T	Adj. % T	D	c	L	Wall
0-L-1	BzOH 0.01842 GW	0	0	86.0	91.5	.037	0.53		
1		400	835	80.0	85.2	.070	1.00	0.463	
2		"	2085	73.6	78.3	.106	1.51		
3		"	4170	61.9	65.9	.181	2.59		
4		"	8350	48.1	51.2	.291	4.16		
5		200	835	81.0	86.2	.064	0.91	0.500	
6		"	2085	72.3	76.9	.114	1.63		
7		"	4170	62.0	66.0	.180	2.57		
8		"	8350	43.7	46.5	.332	4.74		
0-M-1	BzOH 0.00921 GW	0	0	89.0	94.7	.024	0.34		
1		400	835	86.1	91.6	.038	0.54	0.269	
2		"	2085	81.2	86.4	.063	0.90		
3		"	4170	71.8	76.4	.117	1.67		
4		"	8350	63.7	67.8	.169	2.41		
5		200	835	86.1	91.5	.038	0.54	0.284	
6		"	2085	80.2	85.3	.069	0.99		
7		"	4170	73.8	78.5	.105	1.50		
8		"	8350	60.7	64.6	.190	2.71		
0-N-1	BzOH 0.00460 GW	0	0	89.2	94.9	.023	0.33		
1		400	835	87.0	92.6	.033	0.47	0.165	
2		"	2085	83.8	89.2	.049	0.70		
3		"	4170	80.7	85.9	.066	0.94		
4		"	8350	70.7	75.3	.123	1.76		
5		200	835	86.1	91.6	.038	0.54	0.265	
6		"	2085	83.0	88.3	.054	0.77		
7		"	4170	72.1	76.8	.115	1.64		
8		"	8350	63.1	67.2	.173	2.47		
0-o-1	Acet0.01758 GW	0	0	86.5	90.1	.045	0.64		
1		635	@ 400	84.0	87.5	.058	0.83	0.389	
2		1585	"	78.2	81.4	.089	1.27		
3		3170	"	74.3	77.4	.111	1.59		
4		6340	"	52.8	55.0	.260	3.43		
5		635	@ 200	83.0	86.4	.063	0.90	0.495	
6		1585	"	80.0	83.3	.079	1.13		
7		3170	"	63.8	66.4	.178	2.54		
8		6340	"	52.1	54.3	.265	3.79		
0-U-1	BzCH 0.03 GW	0	0	72.6	77.3	.112	1.60		
10-U-1	"	400	8350	29.4	31.3	.505	7.20	0.671	
0-V-1	BzOH	0	0	94.1	100.0				
10-V-1	BzOH	400	8350	93.9					
	Acet	0	0	96.0					

Tab [illegible] III - [illegible]

Tabulation III, Series III 200 Kev X-ray Tests, % T at 6400 A.

No.	S	r/min	rd	% T	Adj. % T	D	c	L	Wall
01-O-3	BzOH .0525MGCN	400	4170	46.5	48.8	.311	4.44	0.944	SW
4	" " MGCN		0	88.1	92.4	.034	0.49		SW
7	BzCH MGCN		0	95.2	100.0				SW
11	BzOH .0525MGCN		4170	44.1	46.5	.332	4.74	1.010	GW
12	" " MGCN		0	87.0	91.8	.037	0.53		GW
13	BzOH MGCN		0	94.8	100.0				GW
01-L-3	BzOH .02 MGH	400	4170	17.4	18.3	.737	10.53	0.077	SW
4	BzOH .02 MGH		0	18.3	19.3	.715	10.21		SW
7	BzOH		0	95.0	100.0				SW
11	BzOH .02 MGH		4170	15.2	16.0	.796	11.36	0.276	GW
12	BzOH .02 MGH		0	18.3	19.3	.715	10.21		GW
13	BzOH		0	95.0	100.0				GW
01-M-3	Acet .02 MGH	400	3170	23.0	24.1	.618	8.83	0.262	SW
4	Acet .02 MGH		0	26.3	27.5	.560	8.00		SW
7	Acet		0	95.5	100.0				SW
11	Acet .02 MGH		3170	16.1	16.9	.773	11.04	0.959	GW
12	Acet .02 MGH		0	26.3	27.6	.560	8.00		GW
13	Acet		0	95.4	100.0				GW
01-N-3	AAE .02 MGH	400	4100	10.8	11.3	.945	15.48	0.386	SW
4	AAE .02 MGH		0	13.5	14.2	.848	13.90		SW
7	AAE		0	95.2	100.0				SW
11	AAE .02 MGH		4170	12.1	12.7	.897	14.70	0.242	GW
12	AAE .02 MGH		0	13.9	14.6	.837	13.71		GW
13	AAE		0	95.4	100.0				GW

Preparation of Pure Malachite Green Leucocyanide.
(4,4' - Tetramethyldiaminotriphenylacetonitrile)

Use only C.P. Reagents and Absolute Solvents.

1) To a cold filtered 1 percent aqueous solution of 2.30 grams of Malachite Green Oxalate, add a cold saturated solution of 1.5 grams of KCN. Collect the precipitate, wash with distilled water.

2) Dissolve the crude precipitate in cold 1% HCl, allow to stand with mixing for one hour. Precipitate carefully with cold 2% NH_4OH. The leucocyanide will precipitate before complete decolorization of the solution. Collect, wash and air dry precipitate at room temperature.

3) Under reduced illumination, (red safelight) dissolve the crude leucocyanide in 100cc of an azeotropic mixture of Ethyl Acetate and Methyl Alcohol (50% by volume), filter. Add 50 cc of Methyl Alcohol, 1cc Acetone, and 1 or 2 drops of Glacial Acetic Acid. Rapidly distil off 110 cc of the mixture, cool the remainder until crystallization, with rapid mixing, is complete. Collect crystals, wash on filter with 10cc Methyl Alcohol. Save filtrate.

4) Repeat (3) seven or eight times to remove all traces of color. Check for free cyanide, with $AgNO_3$, in aq. alcoholic solution. In acidified solution, a precipitate indicates the probable presence of cyanide.

5) Reduce all filtrates by evaporation, as in part (3), recover leucocyanide by (4).

6) After final recrystallization, collect on filter, dry in

vacuum at room temperature. M.P. 176°C. Theor. Yield 1.77gm.
7) This procedure is designed to remove all free cyanide impurities and all undesired color contamination. It will not remove compounds similar in solubility and chemical stability to the leucocyanide. This method of preparation should apply to all of the triphenylmethane dye leucocyanides.

8) A 200 milligram sample of malachite green leucocyanide, recrystallized 3X gave the following analysis:

Melting Point (uncorrected) 178.1-179.8°C.
No Decomposition at 187°C.
Spectrophotometric color at 6400Å measured as 0.01 % by weight as malachite green.

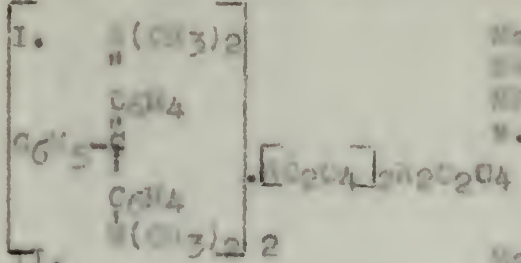
Sample A-81, Reference No. 11197 dated 4 May 1951
Clark Analytical Laboratory
104½ W. Main St., P.O. Box 139, Urbana, Ill.

Dried (room temp.) vac.

	Percent by weight			
	Actual		Average	Theory
C	80.95	81.10	81.02	81.10
H	7.20	6.99	7.10	7.09
N	11.77	11.69	11.73	11.81
Other			0.10	

Tabulation of chemical structures referred to in text, with common and technical nomenclature.

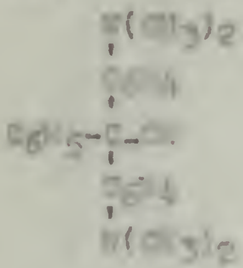
I.



$$\left[\begin{array}{c} N(CH_3)_2 \\ \| \\ C_6H_4 \\ \| \\ C_6H_5-C \\ | \\ C_6H_4 \\ | \\ N(CH_3)_2 \end{array}\right]_2 \cdot [HC_2O_4]^- H_2C_2O_4$$

Malachite Green Oxalate
MW 926.97
MP -----
S. H_2O. Mineral Acids, Org. Solvents.

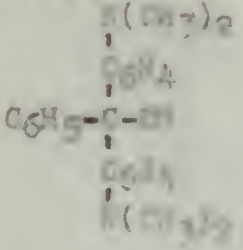
II.



$$\begin{array}{c} N(CH_3)_2 \\ | \\ C_6H_4 \\ | \\ C_6H_5-C-CN \\ | \\ C_6H_4 \\ | \\ N(CH_3)_2 \end{array}$$

Malachite Green Leucocyanide (abbr. MGCN)
(4,4' -tetramethyldiaminotriphenyl-acetonitrile)
M.W. 355.46
M.P. 176°C
I. H_2O Sl.S. MeOH, EtOH
S. Bz, $PhCH_2OH$, EtOAc, AcOH, CCl_4, $CHCl_3$, Aq. mineral acids, Acetone

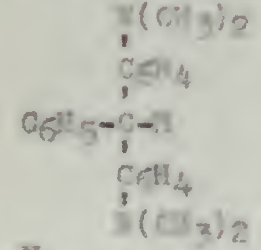
III.



$$\begin{array}{c} N(CH_3)_2 \\ | \\ C_6H_4 \\ | \\ C_6H_5-C-OH \\ | \\ C_6H_4 \\ | \\ N(CH_3)_2 \end{array}$$

Malachite Green Leucocarbinol (Color Base) (Abbr. MGOH)
(4,4' -tetramethyldiaminotriphenyl-carbinol)
M.W. 346.45
M.P. 132°C
I. H_2O Sl.S. MeOH, EtOH
S. (Same as leucocyanide)
Aq. mineral acids -- dye salt.

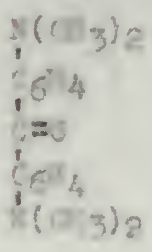
IV.



$$\begin{array}{c} N(CH_3)_2 \\ | \\ C_6H_4 \\ | \\ C_6H_5-C-H \\ | \\ C_6H_4 \\ | \\ N(CH_3)_2 \end{array}$$

Malachite Green Leucobase (Abbr. MGH)
(4,4'-tetramethyldiaminotriphenyl-methane)
M.W. 330.45
M.P. 93°C, 102°C.
Solubility same as leucocyanide.

V.



$$\begin{array}{c} N(CH_3)_2 \\ | \\ C_6H_4 \\ | \\ C=O \\ | \\ C_6H_4 \\ | \\ N(CH_3)_2 \end{array}$$

Michler's Ketone
(Para-dimethylaminobenzophenone)
M.W. 268.35
M.P. 174°C Colorless in benzene.
Solubility same as leucocyanide, but also soluble in dil. alkali.

VI. $C_6H_5-NH-C_6H_5$

Diphenylamine
M.W. 169.22
M.P. 52.9°C.
i. H_2O s. MeOH, EtOH, Bz., Ether, CS_2, Acetone.

VII. C_6H_6

Benzene M.W. = 78.11
d. = 0.879 M.P. = 4.4°C
(Abbr. Bz) B.P. = 80.1°C

VIII. CH_3OH

Methanol M.W. = 32.04
d = 0.792 M.P. = -97.8°C
(Abbr.MeOH) B.P. = 64.7°C

IX. CH_3COOH

Acetic Acid M.W. = 60.05
d. = 1.049 M.P. = 16.7°C
(Abbr.AcOH) B.P. = 118.1°C

X. $(CH_3)_2CO$

Acetone M.W. = 58.08
d. = 0.792 M.P. = -94.6°C
(Abbr.Acet) B.P. = 56.5°C

XI. $C_6H_5CH_2OH$

Benzyl Alcohol
d = 1.043 M.W. = 108.13
(Abbr.BzOH) M.P. = -15.3°C
B.P. = 204.7°C

XII. $CH_3COCH_2COOC_2H_5$

Ethyl Acetoacetate
(Acetoacetic ester)
d. = 1.025 M.W. = 130.14
(Abbr.AAE) M.P. = -45°C
B.P. = 180°C

Appendix C

Reagents and Chemicals used.

(a) Leuco Malachite Green, E.K. Reagent #3626
Eastman Kodak Co., Distillation Products Ind.
(4,4'-Tetramethyldiaminotriphenylmethane)

(b) Malachite Green Oxalate C.I. #657
Allied Chemical & Dye Corp., N.Y., N.Y.
Dye content 98 - 99%
Biological grade.

(c) Tri - Film #9987
General Electric, Schenectady, N.Y.

(d) Benzene, C.P. B.P. - 80.5°C
J.T. Baker Chemical Co.
Phillipsburg, N.J. Thiophene Free.

(e) Malachite Green Hydrochloride
Coleman & Bell Co., Norwood, Ohio

(f) Methyl Alcohol, C.P., ACS, Absolute
Coleman & Bell Co., Norwood, Ohio

(g) Benzyl Alcohol, C.P.
Coleman & Bell Co., Norwood, Ohio

(h) Acetone, C.P.
Coleman & Bell Co., Norwood, Ohio

(i) Ethyl Acetoacetate, C.P.
Eastman Kodak Co., Rochester, N.Y.

(j) Ethyl Acetate, C.P.
Coleman & Bell Co., Norwood, Ohio

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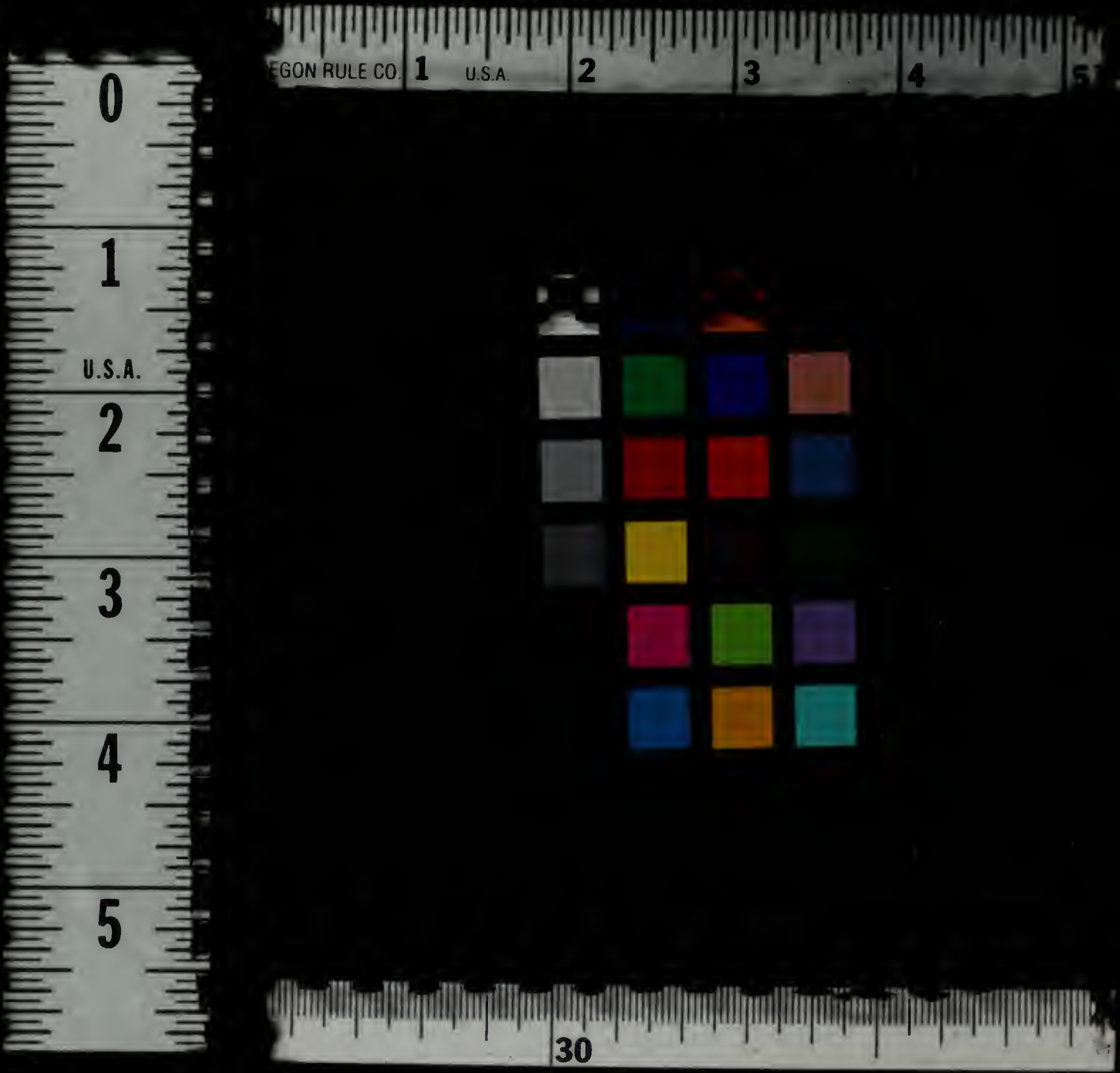
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